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Address correspondence to:

Paul Fuschini (TS-793)
Editorial Manager
Pesticides Monitoring Journal
U. S. Environmental Protection Agency
Washington, D.C. 20460

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HUMANS

Organochlorine Contaminants in Human Milk from Slavonia Province, Yugoslavia, 1978

M. Kodric-Smit,[1] Zdenko Smit,[2] and K. Olie [3]

ABSTRACT

Organochlorine residues were determined in human milk samples from an agricultural area of Slavonia, Yugoslavia. Concentrations of pentachlorobenzene, hexachlorobenzene, α-, β-, γ-isomers of benzene hexachloride, heptachlor, aldrin, DDE, TDE, and DDT were determined by gas chromotography (GC). Confirmation was carried out by computerized GC–mass spectrometry. The most abundant contaminant was p,p'*-DDE (range, 42.0–418.5 μg/kg (ppb)).*

Introduction

For many years, organochlorine pesticides have been investigated because of their toxicity and persistence. Although human milk is the best natural food for babies, it can become a primary depository for organochlorine contaminants. Numerous authors worldwide have reported relatively high levels of these contaminants in human milk (*1, 3–7, 11*).

The present work examines the levels of organchlorine contaminants in the human milk samples from Slavonia Province, Yugoslavia.

Sampling and Analysis

Ten human milk samples were collected at Children's Hospital of Osijek during the first half of 1978. Volunteer donors were lactating mothers, 17 to 41 years old. Samples were manually expressed at one to four months postpartum into precleaned glass bottles. The samples were stored at −30°C until analysis.

Each 10-g milk sample was extracted twice by shaking it for 15 minutes with a mixture of 15 ml acetone and 20 ml hexane. The extract was centrifuged. The hexane layer was collected by pipetting and was concentrated under a stream of nitrogen; the lipids were redissolved in hexane. Cleanup was performed with concentrated H_2SO_4 according to the procedure of Veierov and Aharonson (*10*). Cleaned extracts were analyzed by electron-capture gas chromatography (GC) for the following organochlorine contaminants: pentachlorobenzene, hexachlorobenzene (HCB), α-, β-, and γ-isomers of benzene hexachloride (BHC), heptachlor, aldrin, DDE, TDE, and DDT. Instrument parameters and operating conditions were as follows:

Chromatograph:	Varian Series 1400
Detector:	Sc-H^3 electron capture
Column:	glass, capillary, 0.3 mm × 27 meters, coated with OV-101 after HCl treatment
Split ratio:	1:25
Chromatograph:	Tracor 550
Detector:	Ni^{63} electron capture
Column:	glass, 2 mm × 2 meters, packed with 3 percent SE-30 on 80–100-mesh Chromosorb W-AW

Confirmation was carried out by computerized GC–mass spectrometry (MS) with the following instrument parameters and operating conditions:

GC–MS-Computer System:	Hewlett-Packard 5710A GC and Hewlett-Packard 5980A MS interfaced with Hewlett-Packard 5933A Data System	
Column:	glass, 2 mm × 2 meters, packed with 0.2 percent Carbowax 20M on 100–120-mesh Chromosorb W-AW	
Temperatures, °C:	jet separator	350
	ion source	180
	analyzer	110
Electron energy:	70 eV	
Scan rate:	80 amu/second	

In addition to the usual computer program for GC–MS, the authors used a special program called the halo-test (*8*) for searching organochlorine compounds from stored GC–MS data. The search was performed after each GC–MS run.

Results and Discussion

All samples analyzed contained some of the following organochlorine contaminants: pentachlorobenzene, hexachlorobenzene, α- and β-isomers of BHC, *p,p'*-DDE, *p,p'*-TDE, and *p,p'*-DDT. Results of quantitative deter-

[1] Medicine Center Osijek, Department of Sanitary Chemistry, Drapsinova 1, 54000—Osijek, Yugoslavia.
[2] Faculty of Food Technology, University of Osijek, Zeleno Polje BB, 54000—Osijek, Yugoslavia.
[3] Laboratory of Environmental and Toxicological Chemistry, University of Amsterdam, Amsterdam, The Netherlands.

TABLE 1. *Concentrations of organochlorine contaminants in human milk samples from Slavonia Province, Yugoslavia—1978*

Compound	Sample size, g	Residues, µg/kg	
		Range	Av. Concn
Pentachlorobenzene	6	0–3.4	2.0
Hexachlorobenzene	10	1.6–17.1	5.9
α-BHC	5	<0.1	—
β-BHC	10	4.1–18.6	9.1
p,p'-DDE	10	42.0–418.5	175.7
p,p'-TDE	5	<1	—
p,p'-DDT	10	8.0–135.4	50.8

NOTE: Results are not corrected for recovery. Investigated recovery for the procedure in general was 90–98 percent.

minations of pentachlorobenzene, HCB, β-BHC, *p,p'*-DDE, and *p,p'*-DDT are shown in Table 1.

p,p'-DDE was found most frequently and in the highest concentrations (42.0–418.5 µg/kg).

The best separation of BHC isomers and hexachlorobenzene (HCB) was obtained on the column packed with 0.2 percent Carbowax 20M prepared according to Aue et al. (*2*) which separates isomers of other organochlorine compounds (*9*). Levels of β-BHC, HCB, and pentachlorobenzene were significantly lower than *p,p'*-DDE levels but still high in comparison to levels of α-BHC which was found in traces only. γ-BHC was not found in measurable amounts (detection limit 1 pg), although the most used foodstuffs investigated in our laboratory (unpublished data) and in other laboratories (*12*) contained large amounts of it.

Acknowledgment

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FOOD AND FEED

Residue Dynamics of Acephate and Methamidophos in Urban Dooryard Citrus Foliage, Pompano Beach, Florida—August–September 1978 [1]

George E. Fitzpatrick [2] and Michael D. Bogan [2]

ABSTRACT

Residues of acephate and its toxic metabolite methamidophos, attributable to the State-Federal program for eradication of the citrus blackfly (CBF) [Aleurocanthus woglumi *Ashby*] *on citrus foliage, were assessed in urban areas in Pompano Beach, Florida. Eighteen dooryard citrus trees were sampled on two line transects, each ca 1.6 km long, along two city streets. The trees were sampled twice monthly for five months, beginning before chemical treatments were applied, continuing through the acephate treatment period, and ending when residues decreased below the limits of detection. Acephate and methamidophos residues, as high as 302.5 ppm and 15.8 ppm, respectively, were detected on leaves within one day after the first of a series of three treatments. Significant conversion of acephate to methamidophose was observed. Of the 143 samples collected, 114 contained measurable residues of both compounds; methamidophos accounted for an average of 19 percent of the total residues. Both compounds degraded rapidly, however, and residues averaged below 1 ppm approximately four weeks after the third treatment in the series. Average foliar half-lives for acephate and methamidophos were 8.93 days (SD = 2.52) and 8.40 days (SD = 2.55), respectively.*

Introduction

The citrus blackfly (CBF), *Aleurocantus woglumi* Ashby, was the target of an eradication program conducted jointly by the Florida Department of Agriculture and Consumer Services, Division of Plant Industry (DPI), and the U.S. Department of Agriculture, Animal and Plant Health Inspection Service (APHIS), in southern Florida during 1976–1979. An aleyrodid insect of Asian origin, *A. woglumi* were found as dooryard citrus infestations in the Fort Lauderdale area in early 1976. Other infestations were subsequently discovered throughout Broward County and in Brevard, Dade, Palm Beach, Collier, Martin, Okeechobee, Indian River, and St. Lucie Counties, as well.

Although a number of insecticides had been shown to be effective against *A. woglumi* (*2, 3, 7, 8, 11*), acephate was selected for the eradication program because of acceptable efficacy (*7*), very low acute mammalian toxicity (*5*), and its availability in a soluble powder formulation that would reduce real or potential phytotoxic damage to host plants and other adjacent ornamental plants prevalent in urban areas. Moreover, acephate was shown to have relatively low acute negative impact on biological control agents of *A. woglumi* (*1*).

Although acephate was not registered for CBF control, a crisis exemption was granted by the U.S. Environmental Protection Agency (EPA), allowing its application for citrus blackfly eradication. Acephate was to be applied to all citrus plants as well as mango (*Mangifera indica*) and Surinam-cherry (*Eugenia uniflora*) in Palm Beach, Broward, and Dade Counties. In other Florida counties, only the areas infested were sprayed. It was diluted to 0.6 g/liter and applied with hydraulic sprayers twice at ca 21-day intervals. A third application diluted to 1.6 g/liter was made with a portable backpack mistblower ca 21 days after the second dilute spray.

Since acephate was not registered for this type of use, little data were available on its residue behavior. An earlier study conducted under simulated eradication conditions yielded data on residues in fruit (*6*). In the present study, residues of acephate and its toxic metabolite methamidophos were determined in urban dooryard citrus foliage subjected to insecticide applications during the eradication program. Because the acute toxicity of methamidophos is much greater (acute oral LD_{50} in male rats is 21 mg methamidophos/kg compared to 945 mg acephate/kg) (*5*), residue dynamics of both compounds were assessed.

Materials and Methods

Two line transects, each along a city street, were selected in an urban area of Pompano Beach, Florida. Each transect was ca 10 city blocks long (ca 1.6 km), and

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[2] University of Florida Agricultural Research Center, 3205 S.W. 70th Avenue, Fort Lauderdale, Fla. 33314.

one *Citrus* spp. tree, either *C. sinensis* (orange) or *C. paradisi* (grapefruit), was selected for sampling on each city block. Although homeowner cooperation was secured in advance, there were occasional instances when samples could not be taken due to problems in gaining access to certain backyards.

The trees were sprayed by APHIS or DPI employees as part of their regular duties in the citrus blackfly eradication program. Although APHIS and DPI supervisory personnel cooperated with the residue analysis program, the persons doing the spraying were for the most part unaware of the residue sampling. This was to ensure that the monitoring would be most representative of actual eradication spraying conditions.

Each selected tree was sampled at two-week intervals, from early August until December 1978. Ten to twenty leaves were removed and placed in plastic bags. The filled bags were placed on ice and transported to the laboratory where they were stored at −25°C until analysis. Samples were stored in this manner for 0.5–3.5 months before analysis. The effect of storage on hydrolysis of acephate to methamidophos was not determined.

At the time of analysis, the leaves were thawed and 5-g aliquots were weighed. Each 5-g sample was extracted three times in a Lourdes homogenizer with 50-ml portions of ethyl acetate (150 ml total volume) and 15 g anhydrous Na_2SO_4. Resultant extracts were evaporated to dryness and dissolved in 25 ml ethyl acetate for gas chromatographic (GC) analysis. GC analysis procedures were adapted from earlier studies (*3, 4, 6*). The following instrument parameters and operating conditions were used:

Gas chromatograph:	Tracor Model 222	
Detector:	flame photometric in phosphorus mode	
Column:	glass, 91 cm long by 4 mm ID, packed with 1 percent Reoplex 400 on 80–100-mesh Gas-Chrom Q	
Temperatures:	column:	program initiated 2 minutes after injection, to increase from 140°C to 190°C at 20°C/minute
	inlet:	190°C
	detector:	160°C
Gases:	nitrogen (carrier) flowing at 50 ml/minute; hydrogen at 100 ml/minute; and air at 120 ml/minute	

Calculations for decay curves for acephate and methamidophos on each sampled tree were based on time after the last treatment according to the equation:

$$y = y_o e^{bz} \qquad (1)$$

The date of the last treatment was taken from records kept by the spray crews (Gregory F. Lotorto, January 1979; Florida Department of Agriculture and Consumer Services, Ft. Lauderdale, Fla., personal communication). The decay rates were used to compute $t_{½}$ values for both compounds on each sampled tree when at least three detectable residues were measured after the last treatment and when the correlation coefficient for Equation 1 was at least 0.70 by the equation:

$$t_{½} = \frac{1n(0.5)}{-b} \qquad (2)$$

Results and Discussion

The first detectable foliar residues of acephate and methamidophos in transect 1 were determined on two trees on August 15 and on the other seven trees by August 29 (Table 1). In transect 2, the spraying commenced slightly later; none of the trees had detectable residues on August 15 but all did by August 29 (Table 2).

TABLE 1. *Acephate and methamidophos residues in* Citrus *spp. foliage along N.E. 2nd Street, Pompano Beach, Florida—1978*

Species	Tree No.[1]	Compound	Foliar Residues, ppm Wet Weight										
			Aug. 7	Aug. 15	Aug. 29	Sept. 11	Sept. 26	Oct. 10	Oct. 24	Nov. 7	Nov. 20	Dec. 5	Dec. 19
Citrus sinensis	1–1	Acephate	ND	20.4	5.88	52.8	6.12	10.4	2.15	0.91	0.36	0.21	<0.02
		Methamidophos	ND	4.40	0.52	15.8	1.28	2.00	0.34	0.07	0.04	<0.03	<0.03
	1–3	Acephate	ND	ND	7.35	1.60	6.60	11.5	2.07	0.82	0.04	0.07	0.02
		Methamidophos	ND	ND	1.24	0.49	2.07	2.56	0.86	0.27	<0.03	<0.03	<0.03
	1–5	Acephate	ND	ND	5.60	1.42	3.97	7.80	0.67	0.12	6.42	0.39	0.16
		Methamidophos	ND	ND	1.78	0.25	0.73	0.75	0.22	0.05	1.07	0.12	<0.03
	1–9	Acephate	ND	ND	7.67	M[2]	0.60	2.22	0.44	0.16	0.02	0.17	0.02
		Methamidophos	ND	ND	1.52	M	0.20	0.32	0.12	<0.05	<0.03	0.06	<0.03
Citrus paradisi	1–2	Acephate	ND	ND	9.14	0.87	14.7	19.4	7.25	1.66	0.08	0.06	0.16
		Methamidophos	ND	ND	2.15	0.17	3.28	1.97	2.20	0.48	0.04	<0.03	<0.03
	1–4	Acephate	ND	142.5	11.4	1.01	9.65	21.6	2.67	0.63	0.03	0.07	0.02
		Methamidophos	ND	2.93	1.85	0.33	2.65	2.00	0.62	0.09	<0.03	<0.03	<0.03
	1–6	Acephate	ND	ND	9.52	41.3	1.47	7.00	1.34	0.91	0.07	0.07	<0.02
		Methamidophos	ND	ND	1.89	3.60	0.48	0.29	0.49	0.21	<0.03	<0.03	<0.03
	1–8	Acephate	ND	ND	35.3	1.68	4.04	0.69	0.09	0.39	0.01	<0.02	<0.02
		Methamidophos	ND	ND	2.40	0.38	0.84	0.11	0.12	<0.05	<0.03	<0.03	<0.03
	1–10	Acephate	ND	ND	5.54	305.1	6.30	32.7	10.30	1.60	0.76	0.61	<0.02
		Methamidophos	ND	ND	1.21	15.0	1.29	4.00	2.70	0.27	0.17	0.15	<0.03

NOTE: ND = not detected.
[1] Prefixes 1 or 2 indicate transects 1 or 2.
[2] M = sample not collected.

TABLE 2. *Acephate and methamidophos residues on* Citrus *spp. foliage along N.E. 4th Street, Pompano Beach, Florida—1978*

Species	Tree No. [1]	Compound	Foliar Residues, ppm Wet Weight									
			Aug. 15	Aug. 29	Sept. 11	Sept. 26	Oct. 10	Oct. 24	Nov. 7	Nov. 20	Dec. 5	Dec. 19
Citrus sinensis	2–1	Acephate	ND	4.53	3.49	20.1	12.2	2.42	0.24	0.07	0.09	0.04
		Methamidophos	ND	0.11	1.25	1.90	1.64	1.20	0.12	<0.02	<0.03	<0.03
	2–4	Acephate	ND	302.5	M [2]	3.85	0.13	0.04	0.15	0.09	0.03	0.02
		Methamidophos	ND	11.00	M	1.20	0.03	0.04	0.12	0.06	<0.03	<0.03
	2–5	Acephate	ND	7.14	0.68	6.00	11.3	0.29	0.12	0.07	0.02	<0.02
		Methamidophos	ND	1.20	0.25	1.55	1.29	0.07	<0.03	<0.02	<0.03	<0.03
Citrus paradisi	2–2	Acephate	ND	M	7.72	34.8	8.44	3.07	0.14	0.19	0.07	0.10
		Methamidophos	ND	M	1.18	2.68	1.59	0.97	0.05	<0.02	<0.03	<0.03
	2–3	Acephate	ND	M	1.39	1.83	13.8	3.86	2.15	0.23	0.08	<0.02
		Methamidophos	ND	M	0.32	0.43	2.22	0.59	0.49	<0.02	<0.03	<0.03
	2–6	Acephate	ND	12.3	1.07	13.7	1.06	2.50	0.11	0.18	0.08	<0.02
		Methamidophos	ND	2.17	0.24	1.83	0.22	0.58	0.03	0.05	<0.03	<0.03
	2–7	Acephate	ND	9.93	1.01	3.69	15.8	2.36	0.11	0.14	<0.02	0.02
		Methamidophos	ND	1.86	0.25	1.45	0.63	0.48	0.05	<0.02	<0.03	<0.03
	2–8	Acephate	ND	137.8	8.01	5.44	1.68	3.31	0.70	1.77	0.17	<0.02
		Methamidophos	ND	6.25	1.40	2.35	0.40	1.34	0.18	0.67	0.06	<0.03
	2–9	Acephate	ND	10.7	6.08	3.56	1.85	0.25	0.05	0.05	0.14	<0.02
		Methamidophos	ND	1.91	1.14	1.12	0.33	0.10	<0.03	<0.02	0.05	<0.03

NOTE: ND = not detected.
[1] Prefixes 1 or 2 indicate transects 1 or 2.
[2] M = sample not collected.

TABLE 3. *Acephate application dates for the* Citrus *spp. trees in both transects, Pompano Beach, Florida—1978*

Tree No.[1]	Species	Application Date		
		First	Second	Third
1–1	*Citrus sinensis*	Aug. 10	Sept. 6	Sept. 28
1–3		Aug. 18	Sept. 14	Oct. 4
1–5		Aug. 17	Oct. 4	Nov. 7
1–9		Aug. 18	Sept. 12	Oct. 2
1–2	*Citrus paradisi*	Aug. 18	Sept. 14	Oct. 4
1–4		Aug. 23	Sept. 19	Oct. 6
1–6		Aug. 14	Sept. 7	Sept. 28
1–8		Aug. 24	Sept. 15	Oct. 2
1–10		Aug. 17	Sept. 11	Sept. 29
2–1	*Citrus sinensis*	Aug. 28	Sept. 15	Oct. 5
2–4		Aug. 29	Sept. 20	NS [2]
2–5		Aug. 21	Sept. 15	Oct. 5
2–2	*Citrus paradisi*	Aug. 28	Sept. 15	Oct. 5
2–3		Aug. 21	Sept. 13	Oct. 2
2–6		Aug. 23	Sept. 19	Oct. 11
2–7		Aug. 23	Sept. 19	Oct. 9
2–8		Aug. 28	Sept. 22	Oct. 13
2–9		Aug. 21	Sept. 13	Oct. 2

NOTE: Information supplied by G. L. Lotorto, Florida Department of Agriculture and Consumer Services, Fort Lauderdale, Florida.
[1] Prefixes 1 or 2 indicate Transect 1 or 2.
[2] NS = not sprayed.

With one exception, all trees in both transects were sprayed during the period August 10 to October 13 (Gregory F. Lotorto, January 1979; Fort Lauderdale, Fla., personal communication). The actual spray application dates are shown in Table 3. The one exception was tree 1-5 in transect 1, which was apparently overlooked initially by the spray crews and treated later when the oversight was detected. That tree received its third treatment on November 7 and this later treatment accounts for the apparent protraction of its residues evident in Table 1.

In most cases, acephate residues remained above 1 ppm during the two-month treatment period and for ca one month after the treatment period (Tables 1 and 2). The highest concentrations of both compounds were detected in samples taken during the first month of the treatment period, when some trees had residues exceeding 300 ppm acephate and 15 ppm methamidophos. The first month of the treatment period encompassed the two treatments applied as dilute sprays, whereas the third treatment, applied by mist-blower, produced lower residue values. This agrees with earlier work in which acephate and methamidophos were not detected in fruits of citrus plants treated by mist-blower application but were detected in fruits of trees treated with dilute sprays applied by hydraulic equipment (*6*). Apparently, the higher concentration coupled with less aqueous carrier results in less toxicant deposition on leaf surfaces as well as lower uptake into the fruit.

Residue values for both compounds measured after the last of the series of three treatments were used to assess the rates of decay on foliage (Table 4). The average half-lives of acephate and methamidophos on citrus foliage were 8.93 days and 8.40 days, respectively, with no pronounced difference between the two plant species. These values can be compared with half-lives of 10.3 days and 10.5 days for acephate and methamidophos, respectively, in the rind of oranges, grapefruit, lemons, and tangerines, and half-lives of 15.0 days and 6.1 days for acephate and methamidophos, respectively, in citrus pulp (*6*). In contrast, half-lives of acephate and methamidophos in needles of Douglas fir (*Pseudotsuga menziessii*) were reported in one study to be ca three days for each compound (*10*) and in another study, ca five days for each compound (*9*). In all of the above-mentioned studies as in the present study, only acephate was applied, and methamidophos residues, when de-

TABLE 4. *Decay dynamics of acephate and methamidophos on urban dooryard* Citrus *spp. trees, Pompano Beach, Florida—1978*

Tree No.[1]	Species	Acephate $t_{1/2}$, Days	Acephate N	Acephate r	Methamidophos $t_{1/2}$, Days	Methamidophos N	Methamidophos r
1–1	*Citrus sinensis*	−9.90	5	−0.98	−6.98	4	−0.98
1–3		−7.67	4	−0.88	[2]	2	[2]
1–5		−5.31	3	−0.96	[2]	2	[2]
1–9		−11.50	5	−0.75	[2]	2	[2]
2–1		−8.63	6	−0.93	−7.67	3	−0.92
2–4		−13.80	7	−0.79	[2]	5	−0.50
2–5		−6.90	5	−0.93	[2]	2	[2]
		$\bar{x}$ = −9.10			$\bar{x}$ = −7.29		
		SD = 2.89			SD = 0.54		
1–2	*Citrus paradisi*	−8.63	6	−0.90	−6.90	4	−0.91
1–4		−6.27	5	−0.94	−6.27	3	−0.99
1–6		−7.67	5	−0.96	[2]	3	−0.38
1–8		−8.63	4	−0.76	[2]	2	[2]
1–10		−8.63	5	−0.96	−9.86	5	−0.93
2–2		−9.86	6	−0.89	−5.75	3	−0.92
2–3		−6.90	5	−0.98	−13.80	3	−0.92
2–6		−9.86	4	−0.81	−7.67	3	−0.79
2–7		−5.31	4	−0.94	−7.67	3	−0.91
2–8		−11.50	4	−0.81	−11.50	4	−0.76
2–9		−13.80	5	−0.71	[2]	2	[2]
		$\bar{x}$ = −8.82			$\bar{x}$ = −8.68		
		SD = 2.41			SD = 2.81		
	Grand mean	$\bar{\bar{x}}$ = −8.93			$\bar{\bar{x}}$ = −8.40		
		SD = 2.52			SD = 2.55		

NOTE: Correlation coefficients (r) for the decay equation $y = y_0 e^{bx}$ were computed when the number of data points (N) after the last treatment was equal to or greater than 3. Half-life values for each tree ($t_{1/2}$) were computed when $r \geq 0.70$.

[1] Prefixes 1 or 2 indicate transect 1 or 2.

[2] Value not computed. See text for explanation.

TABLE 5. *Average composition of total residue (acephate plus methamidophos) expressed as either compound, based on residues listed in Tables 1 and 2*

Species	Transect	Acephate $\bar{x}$	Acephate SD	Acephate N	Methamidophos $\bar{x}$	Methamidophos SD	Methamidophos N
Citrus sinensis	1	0.81	0.06	27	0.19	0.06	27
	2	0.77	0.14	17	0.23	0.14	17
Citrus paradisi	1	0.82	0.10	33	0.18	0.10	33
	2	0.81	0.07	37	0.19	0.07	37
Total		0.81	0.09	114	0.19	0.09	114

tected, were presumed to be the result of hydrolysis of acephate.

In the data shown in Tables 1 and 2, a total of 114 samples contained measurable residues of both acephate and methamidophos. Twenty-nine contained acephate only (generally at levels approaching the limits of detection), and the remainder did not contain any measurable residues of either compound. Since the conversion of acephate to the more toxic methamidophos is a potential environmental problem, attention was given to the relative proportions of each compound expressed as a function of the total residue in each sample (Table 5). On the average, 81 percent of the total residue (acephate plus methamidophos) was in the form of acephate, with an average of 19 percent methamidophos. There were no pronounced differences between citrus species or between plots (Table 5), and the variability was quite low (SD $<<\bar{x}$).

Although there is significant conversion of acephate to its more toxic metabolite, methamidophos, in *Citrus* spp. leaves, the rapid disappearance of both compounds can reduce risk of exposure to dangerous levels of toxicant.

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FISH, WILDLIFE, AND ESTUARIES

Organochlorine Residues in Eggs of Loggerhead and Green Sea Turtles Nesting at Merritt Island, Florida—July and August 1976

Donald R. Clark, Jr., and Alexander J. Krynitsky [1]

ABSTRACT

Eggs from nine clutches of loggerhead turtles (Caretta caretta) *and two clutches of green turtles* (Chelonia mydas) *were collected as they were laid on Merritt Island, Florida. Eggs were incubated, frozen, and analyzed for organochlorines.*

Levels of DDE and PCB, the major contaminants, averaged less than 0.08 ppm in loggerhead eggs and were even lower in green turtle eggs. These concentrations are far below levels thought to be potentially harmful. Loggerhead eggs were frozen after 43–52 days incubation; both DDE and PCB declined significantly during this interval. Authors estimate that DDE averaged about 0.2 ppm in loggerhead eggs when they were laid.

DDE levels in eggs of both turtle species were less than levels in eggs of crocodiles (Crocodylus acutus) *from Everglades National Park and in eggs of 13 species of aquatic birds nesting on Merritt Island. The remarkably low residues in the turtle eggs probably indicate that, when not nesting, the turtles live and feed in areas remote from Florida.*

Introduction

Declining populations of marine turtles throughout the world are attributable to the taking of both adults and eggs for sale or for immediate consumption as food (*3*). In the United States, human destruction of nesting beaches and predation on eggs by raccoons (*Procyon lotor*) are also major factors (*3*). Both loggerhead (*Caretta caretta*) and the green turtle (*Chelonia mydas*) have been classified recently as "threatened," and the Florida breeding population of the green turtle has been listed as "endangered" (*11*).

Whether chemical pollution threatens marine turtles is uncertain. Eggs of the predominantly herbivorous green turtle from Ascension Island contain only very low organochlorine residues (*10*). Residues in eggs of the more carnivorous loggerhead turtle from Georgia and South Carolina appear to be somewhat higher (*8*), but data are presented in such a way that precise comparisons are not possible. The present study examined eggs of loggerhead and green turtles collected in Florida.

Materials and Methods

Entire clutches from nine loggerhead and two green turtles were collected as they were laid on the Canaveral National Seashore and the adjacent Merritt Island National Wildlife Refuge (MINWR), Brevard County, Florida. All 11 clutches were laid between July 13 and August 6, 1976. Clutch size averages more than 100 eggs in both species (*6*). At laying, 20 eggs from each loggerhead clutch and five from each green turtle clutch were selected randomly, weighed, and numbered using India ink so that toxicant levels measured later could be related to original weights of eggs. Each clutch was placed in a plastic container, covered with sand, and incubated in a laboratory (house trailer) which was open to the ambient temperature and humidity of the beach.

Clutches were dug up after intervals of 43, 45, 48, 49, or 52 days. The numbered eggs were weighed again, wrapped individually in aluminum foil, sealed in plastic bags, and frozen. The remainder of each clutch was incubated until all viable eggs had hatched; these hatchlings were released to the ocean. Eggs that did not hatch (3–10 per loggerhead clutch, 8 and 13 for green turtle clutches) were placed with others from the same clutch that had been frozen previously. Eggs were frozen after a 43–52-day incubation period because, after that length of time, eggs with living embryos could be easily distinguished from eggs in which no embryo had developed. The experimental design called for comparison of residue levels in fertile and infertile eggs.

All eggs were packed in Dry Ice and shipped to the Patuxent Wildlife Research Center (PWRC) where they were weighed and opened, and the straight-line carapace

[1] Fish and Wildlife Service, U.S. Department of the Interior, Patuxent Wildlife Research Center, Laurel, Md. 20811.

length of each embryo was measured with a vernier caliper. Contents of each egg minus the shell were placed in separate, tared glass jars that had been cleaned with acetone and hexane, and the jars and contents were weighed. Subsequently, each sample egg was homogenized in a blender and analyzed for organochlorines.

Loggerhead eggs frozen after 43–52 days of incubation either contained well developed embryos (mean embryo carapace lengths of samples from nine clutches ranged from 32.3 mm to 37.4 mm) or showed no embryonic development and were classified as infertile. The rate of infertility in each 20-egg sample ranged from 5 percent to 25 percent (1–5 eggs) and averaged 12 percent. All 10 green turtle eggs frozen after 43–52 days of incubation contained large embryos. Carapace lengths averaged 37.6 mm and 39.2 mm for the two clutches.

Unhatched loggerhead eggs frozen after viable eggs had hatched also either contained large embryos or were infertile. Percentages of infertile eggs were higher, ranging from 33 percent to 100 percent and averaging 69 percent. Unhatched green turtle eggs frozen after viable eggs had hatched were 90 percent and 100 percent infertile.

To make a statistical comparison of residue levels in fertile versus infertile loggerhead eggs, authors randomly selected and analyzed 10 fertile eggs from among the 20 per clutch that were frozen after 43–52 days of incubation. Then, for comparison, authors analyzed all infertile eggs from that same clutch plus all available infertile eggs frozen after the rest of the clutch hatched to a maximum combined total of 10 eggs. Green turtle clutches were treated similarly except that only five fertile eggs were analyzed from each clutch.

At an analytical sensitivity of 0.1 ppm for organochlorine pesticides and 0.5 ppm for polychlorinated biphenyls (PCBs), 107 of 170 loggerhead eggs (63 percent) and all 28 green turtle eggs contained no measurable residues. Among loggerheads, samples from three clutches contained no measurable residues, samples from two clutches had only one egg with residues, and the sample from one clutch had only three eggs with residues. Measurable residues were limited to DDE and PCB. Authors analyzed a second subsample from one fertile egg of each clutch at a sensitivity of 0.005 ppm for organochlorine pesticides and 0.025 ppm for PCBs. Residues discussed hereafter are from these 11 more sensitive analyses unless indicated otherwise.

For each analysis, a 10-g portion of the homogenized egg was mixed with anhydrous sodium sulfate and extracted for 7 hours in a Soxhlet apparatus. Extraction, sample cleanup, and separation of organochlorine pesticides from PCBs were performed as described by Cromartie et al. (*5*), except that the SilicAr separation was collected in four fractions to facilitate separation of endrin and dieldrin. The fractions were analyzed on a Hewlett-Packard Model 5753 gas-liquid chromotograph equipped with a ^{63}Ni detector, automatic sampler, and computing integrator. Instrument characteristics and operating conditions follow:

Column:	glass, 1.83 meters, packed with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1	
Temperatures:	column	200°C
	detector	300°C
	injection port	250°C
Carrier gas:	5 percent methane in argon flowing at 60 ml/minute; purge flow, 40 ml/minute	

Samples were analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, endrin, heptachlor epoxide, mirex, oxychlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, and PCBs. Recovered PCB always resembled Aroclor 1260.

Average percentage recoveries from spiked chicken (*Gallus gallus*) egg tissue ranged from 83 percent to 104 percent. Residue data were not adjusted on the basis of these recoveries. Authors confirmed residues in one of the 11 samples analyzed at high sensitivity, using a Finnigan Model 4000 gas-liquid chromatograph–mass spectrometer in the selective ion mode.

Geometric means and 95 percent confidence intervals are given for residues because the data were positively skewed, but they were calculated only for those residues (DDE and PCB) that occurred in a majority of samples in a series. Arithmetic means and standard errors are also given where comparison with similarly derived means from other studies is required.

Results and Discussion

GENERAL LEVELS OF RESIDUES

Residues of eight organochlorine compounds were recovered from eggs of loggerhead turtles, but only DDE and DDT were found in eggs of the green turtle (Table 1). Green turtle eggs from Ascension Island contained

TABLE 1. *Organochlorine residues in nine loggerhead and two green turtle eggs from Merritt Island National Wildlife Refuge, Florida—July and August 1976*

Chemical	Number with Residues	Residues, ppm Wet Weight: Geometric Mean	95% CI	Range
LOGGERHEAD TURTLE EGGS				
DDE	9	0.047	0.024–0.090	0.018–0.200
DDT	2			ND–0.048
Dieldrin	4			ND–0.028
Heptachlor epoxide	2			ND–0.006
Oxychlordane	2			ND–0.017
trans-Nonachlor	1			ND–0.009
Mirex	1			ND–0.005
PCB (Aroclor 1260)	9	0.078	0.047–0.130	0.032–0.201
GREEN TURTLE EGGS				
DDE	1			ND–0.005
DDT	1			ND–0.042

NOTE: CI = confidence interval; ND = not detected.

only DDE and PCB residues (*10*). In an unspecified number of loggerhead eggs from Georgia and South Carolina, ΣDDT ranged from 0.058 ppm to 0.305 ppm and dieldrin from a trace to 0.056 ppm; embryos apparently were not observed (*8*). These latter results seem similar to the present results, but precise comparisons are not possible.

LEVELS OF DDE AND PCB COMPARED TO DAYS OF INCUBATION

Even though the range of incubation periods for loggerhead clutches was only nine days (43–52 days of incubation) the concentrations of DDE and PCB declined significantly during this time (Fig. 1). Residue data were also plotted as total micrograms per egg and as ppm wet weight of the whole egg at laying to avoid the possibility of confusing dilution through the uptake of water by the egg with actual loss of residues; significant regressions similar to Figure 1 were obtained: total μg DDE, $r = -0.743$, $0.05 > P > 0.02$; total μg PCB, $r = -0.850$, $0.01 > P > 0.001$; ppm DDE at laying, $r = -0.747$, $0.05 > P > 0.02$; ppm PCB at laying, $r = -0.790$, $0.02 > P > 0.01$. Uptake of water during this 10-day portion of incubation was probably negligible because there was no significant increase in egg weights.

Authors believe that DDE and PCB declined because a portion of these compounds present at laying was metabolized by the developing loggerhead embryos to compounds not measured by the analytical methods. Such metabolism (DDE to DBP, or 4,4′-dichlorobenzophenone) has been demonstrated in developing chicken embryos (*1*). If the linear relationships in Figure 1 are extrapolated backward, then mean levels at laying can be estimated at ca 0.9 ppm. However, because embryos metabolize the stored fat, and hence the DDE and PCB, of the egg more rapidly as they become larger and their needs become greater, the relationships of Figure 1 would not be linear over the entire incubation period. That is, the 10-day interval shown in Figure 1 constitutes 15.5 percent of the incubation period; complete incubation averaged 64.5 days (S. Vehrs, 1979, MINWR; personal communication). But the amount of metabolism during the 10 days must have been greater than 15.5 percent. Thus the amount of DDE in eggs at laying must have been less than 0.9 ppm.

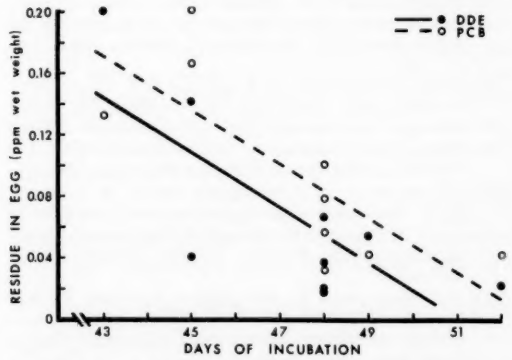

FIGURE 1. *Relationship of residue concentration to length of incubation period among nine loggerhead turtle eggs, each from a different clutch. For DDE,* $r = -0.753$, $0.02 > P > 0.01$; *and for PCB (Aroclor 1260),* $r = -0.772$, $0.02 > P > 0.01$.

To estimate DDE levels in loggerhead eggs at laying, authors used quantifications from infertile eggs because no DDE could have been metabolized. Infertile eggs were analyzed only at the 0.1 ppm sensitivity, so authors selected the three clutches in which DDE was quantified for all eggs in order to assure the most accurate analytical readings. Authors calculated arithmetic means for the infertile eggs in those clutches. The results were 0.252 ± 0.026 ppm ($n = 10$); 0.268 ± 0.057 ppm ($n = 5$); and 0.222 ± 0.040 ppm ($n = 4$). Because these means are an upwardly biased estimate of levels at laying (results are from the three most contaminated clutches), authors believe the actual value was somewhat lower, perhaps ca 0.2 ppm.

DDE LEVELS IN SEA TURTLE EGGS FROM FLORIDA COMPARED WITH DDE LEVELS IN EGGS OF CERTAIN OTHER POPULATIONS

DDE is well known for its adverse effect on the reproduction of several bird species. However, the lowest concentration in eggs known to affect the brown pelican (*Pelecanus occidentalis*), which may be the most sensitive species, is 2.5 ppm (*2*). DDE concentrations in the Florida sea turtle eggs are far below this level (Table 1).

The level of DDE in green turtle eggs in the present study was very similar to that reported for green turtle eggs from Ascension Island (Table 2). However, the eggs from Ascension contained no embryos visible to the naked eye (N. Thompson, 1979, University of Florida, Gainesville, Fla.; personal communication). If eggs in the present study had been analyzed at a similar early stage of development, DDE levels would probably have exceeded those in Ascension Island eggs.

Loggerhead eggs contained substantially more DDE than did green turtle eggs (Table 2). When we consider

TABLE 2. *Residues of DDE in eggs from five reptile and bird populations*

Population	*n*	DDE, ppm Wet Weight: Arithmetic Mean ± SE	DDE, ppm Wet Weight: Range	Ref.
Loggerhead turtle (Florida)	9	0.066 ± 0.021	0.018–0.200	Present study
Green turtle (Florida)	2	0.002 ± 0.002	ND–0.005	Present study
Green turtle (Ascension Island)	10	0.003 ± 0.001	ND–0.009	(*10*)
Crocodile (Florida)	23	1.19 ± 0.15	0.28–3.2	(*7*)
White ibis (Florida)	10	0.29 ± 0.08	ND–0.84	(*9*)

NOTE: SE= standard error; ND = not detected.

the reductions that have probably occurred due to incubation of the Florida eggs, the data in Table 2 suggest that both the contrasting food habits of the two species and the different geographic locations (Ascension Island and Florida) affected DDE levels. The difference in nesting location is related to differences in primary feeding locations. When not nesting, the Ascension Island turtles feed along the Atlantic coast of Brazil (*4*). No one knows where the Florida turtles feed when not nesting, but if organochlorine pollutants in their food species near Florida are high, these pollutants could produce levels in their eggs that exceed levels in eggs from turtles that feed near Brazil.

Eggs of crocodiles (*Crocodylus acutus*) from Everglades National Park contained no visible embryos when prepared for chemical analysis (*7*). DDE concentrations in these eggs (Table 2) were about six times greater than DDE concentrations estimated to have been in loggerhead eggs at laying. The loggerhead eggs had lower DDE residues even though both species are large, carnivorous, marine-estuarine reptiles found in Florida.

Eggs of Florida sea turtles also contained lower residues than did eggs of aquatic birds nesting on MINWR. Eggs of the white ibis (*Eudocimus albus*) contained the lowest DDE residues (Table 2) among 13 species of aquatic birds whose eggs were collected at MINWR (*9*). Most of the white ibis eggs contained small embryos, but the only two with feathered embryos contained 0.12 ppm and 0.18 ppm DDE and three showing no embryonic development contained 0.50, 0.34, and 0.84 ppm DDE (H. Ohlendorf, 1979, PWRC; personal communication). Thus DDE levels in white ibis eggs with large embryos exceeded levels in turtle eggs with large embryos (Table 2), and DDE levels in white ibis eggs showing no embryonic development exceeded levels estimated to have been present in loggerhead eggs at laying.

In summary, the residue concentrations in loggerhead and green turtle eggs from Florida are remarkably low. These low levels probably reflect low dietary intake. The importance of this factor is suggested by the difference in DDE levels in eggs between the two species. Furthermore, the relatively low residue levels in turtle eggs in the present study compared with eggs of crocodiles and aquatic birds probably indicate that when not nesting the turtles live in areas remote from Florida. Such a pattern, with primary feeding sites and nesting sites distant from each other, is common among sea turtles (*3*).

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Accumulation of Polychlorinated Biphenyls in American Shad During Their Migration in the Hudson River, Spring 1977

Michael Pastel,[1] Brian Bush,[2] and Jai S. Kim [1]

ABSTRACT

Fifty-two female American shad (Alosa sapidissima) *were collected during the spring of 1977 at two sites on the lower Hudson River, 27 miles and 75 miles from the river mouth. The fish were extracted with hexane, and the extracts were analyzed by electron-capture gas chromatography (EC-GC) and by GC/mass spectrometry (MS). PCBs were quantitated by EC-GC, and the concentrations were compared by fish length and by site. Fish collected from the downstream site contained a mean PCB concentration of 2.0 ± 1.0 μg/g, wet weight; fish from the upstream site contained a mean PCB concentration of 6.1 ± 2.6 μg/g, wet weight. Aliquots of the hexane extracts were fractionated before analysis by GC/MS. The presence of PCBs was confirmed, and DDE and the alkane series from C_{23} through C_{36} were detected. American shad are saltwater fish that only enter fresh water to spawn. Because they do not feed in fresh water before spawning, they may be used as an indicator of water contamination.*

Introduction

Toxic trace contaminants such as polychlorinated biphenyls (PCBs) permeate the Hudson River (*6*). There are several methods available to monitor this contamination, involving the collection of various samples, such as water, sediments, plants, turtles, macroinvertebrates, fish, and aquatic mammals. For the present study, migratory fish were chosen. American shad (*Alosa sapidissima*) are saltwater fish that enter fresh water only to spawn. They do not eat in fresh water before spawning (*4*); therefore any contamination enters their bodies directly from the water.

This paper presents the results of analyses of fish collected during the spring of 1977. Quantitative results for PCBs are reported, and other compounds are identified.

Sampling and Analysis

SAMPLE PREPARATION

Fifty-two female shad were collected by the New York State Department of Environmental Conservation (DEC) at two sites on the Hudson River and were tagged with an identification number. Twenty were from a site near the Tappan Zee Bridge, and 32 were from a site at Poughkeepsie (27 miles and 75 miles, respectively, from the river mouth), as indicated in Figure 1. Each fish was scaled, beheaded, definned, deboned, gutted, and then homogenized in a Model CFP5 Cuisinart food processor. A 5.0-g subsample from each fish was frozen and lyophilized for 12 hr, and then extracted with 100 ml hexane in a Soxhlet extractor for 2 hr. The extract was quantitatively transferred to a Kuderna-Danish apparatus and concentrated to about 5 ml. The

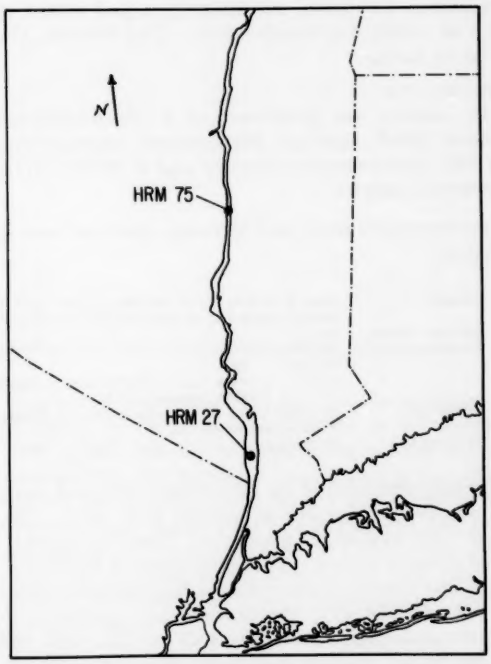


FIGURE 1. *Map of Hudson River sampling sites, for American shad, spring 1977.*

[1] Department of Atmospheric Science, State University of New York at Albany, 1400 Washington Ave., Albany, N.Y. 12222.
[2] Division of Laboratories and Research, New York State Department of Health, Albany, N.Y. 12201.

concentrate was diluted to 10.0 ml of which 2.0 ml was used for electron-capture gas chromatography (EC–GC) and 8.0 ml was used for GC/mass spectrometry (MS). All of the fish were subjected to EC–GC analysis, and 25 were further analyzed by GC/MS.

CLEANUP

A 2.0-ml aliquot of extract for each fish was passed through a column containing 10.0 g of 2 percent deactivated 60–100-mesh Florisil topped with 2.0 g sodium sulfate. The Florisil was activated by heating at 450°C for 4 hr and was cooled in a desiccator. Fifty-gram aliquots were placed in an Erlenmeyer flask which was mounted on a wrist-action shaker. While the flask was shaken at low speed, 1.0 ml distilled-deionized water was added dropwise. Shaking was continued at high speed for 30 min. The aliquots of 2 percent deactivated Florisil were stored in glass jars which were sealed with Teflon lids. Purity was checked by placing 10.0 g of the combined batches in a glass column and eluting the column with 50 ml hexane. The eluate was collected and concentrated to 1.5 ml in a Kuderna-Danish apparatus, and then analyzed by electron-capture GC as described for the sample analysis.

The extract-charged column was eluted with ca 50 ml hexane, and the first 40 ml of eluate was collected. PCBs are eluted with this volume, but more polar compounds, such as DDT and triglycerides, are retained on the column (*5*). The eluate was concentrated in the same manner as the extract, and diluted to a final volume of 1.5 ml, which was transferred to a 2-ml Wheaton GC vial for analysis.

GC ANALYSIS

GC analysis was performed on a Hewlett-Packard Model 5840A digital gas chromatograph equipped with a ^{63}Ni electron-capture detector and a Model 7617A automatic sampler.

Instrument parameters and operating conditions were as follows:

Column:	glass, 6 ft long by 2 mm ID, packed with 1 percent Apiezon L on 100–120-mesh Supelcoport	
Injection volume:	5.0 µl	
Temperatures, °C:	injection	225
	detector	300
	oven	held 5 min at 160°C, then increased 10°C/minute to 220°C
Carrier gas:	ultra high purity argon–methane (95+5), flowing at 18 ml/minute	
Total run time:	38 minutes	

The microprocessor of the EC–GC was calibrated, using a mixture of 4 µg each of Aroclors 1016, 1221, 1254, and 1260/ml plus 0.2 µg mirex/ml. These four commercial mixtures contain the complete range of PCB homologs and isomers produced by the iron-catalyzed chlorination method (*1*). The inclusion of Aroclors with intermediate chlorine contents, such as 1232, 1242, and 1248, would have resulted in overly complicated patterns. Twenty-six peaks were resolved in the standard mixture (Fig. 2) and assigned to their Aroclors of origin (Table 1) by comparison with individual Aroclor chromatograms. The major PCB isomer component of each peak was determined using the procedure reported previously (*2*) by comparison with the retention time data of Sissons and Welti (*10, 14*) and Jensen and Sundstrom (*7*).

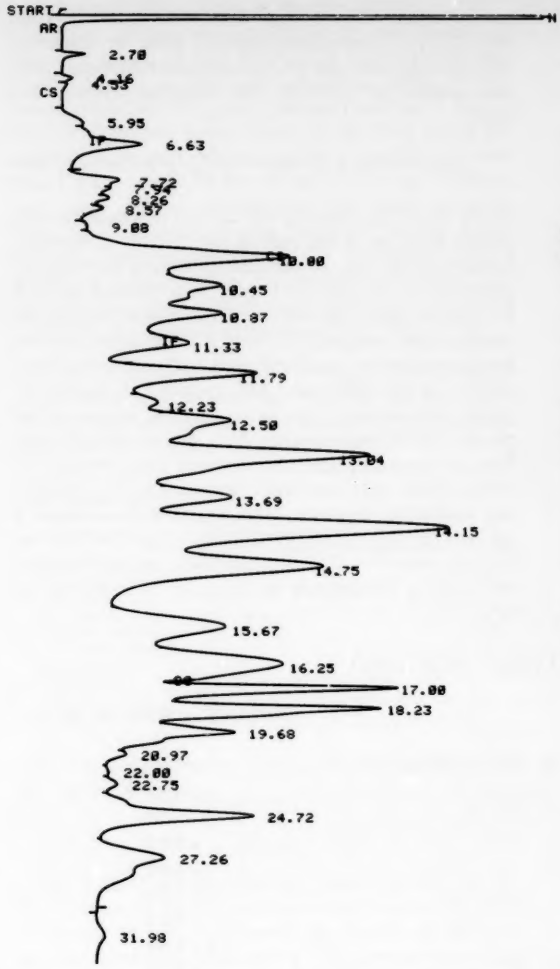
Quantitation was effected on a peak-to-peak basis. Eleven individual homologs, denoted in Table 1, were each analyzed at range of concentrations (0.5–4.0 µg/ml) in order to calculate a response factor. The response factors were normalized as area (integrator counts)/concentration (0.1 µg/ml). The logarithm of the average response factors for each group of isomers (i.e., the same number of chlorine atoms per molecule) was graphed versus the chlorine number (Fig. 3). The resulting curve was nearly linear (correlation factor $\rho = 0.95$). Analysis by the method of least squares (*9*) yields a straight line which was used to estimate response factors for the remainder of the peaks in the standard mixture. These factors were programmed into the GC microprocessor, and the resulting amounts calculated by the microprocessor were summed and compared to the true value of the standard solution. Standard solutions of each of the four Aroclor mixtures were also analyzed. By use of an iterative approach, the response factors were adjusted, the microprocessor was reprogrammed, and the standard solutions were reanalyzed.

Recovery studies were performed by separately spiking 5.0-g (wet weight) portions of uncontaminated fish

TABLE 1. *Peak assignments for PCB standard, 4 µg/ml each of Aroclors 1016, 1221, 1254, and 1260*

Retention Time, Min.	Cal No.	µg/ml in 16 µg/ml 1221, 1016, 1254, 1260 (1:1:1:1)	Major Component of Peak	Major Contributing Aroclor Mixture
2.73	2	1.47	2*	21
4.21	3	1.55	2,2'*†+4*†	16 + 21
6.64	4	1.46	2,4'*	16 + 21
7.78	5	0.53	2,2',5'*†	16 + 21
8.30	6	0.48	2,2',4'	16
8.63	7	0.42	2,2',3'	16 + 21
10.05	8	1.97	Cl_3	16
10.55	9	0.37	2,5,2',5'*+2,3,2',5'*†	16 + 54
10.95	10	0.25	2,3,2',3'*†	16 + 54
11.41	11	0.17	Cl_4	16 + 54
11.89	13	0.37	2,5,2',3',6'	16 + 54 + 60
12.33	14	0.56	Cl_4	54
12.60	15	0.23	2,5,3',4'*	16 + 54
13.19	16	0.33	2,5,2',4',5'†	54 + 60
13.83	17	0.24	2,5,2',3',4'†	54 + 60
14.33	18	1.70	2,3,4,3',6'+Cl_5	54 + 60
14.96	20	0.93	2,3,6,2',4',5'	54 + 60
15.89	21	0.39	2,3,4,2',3',6'	54 + 60
16.46	22	1.12	3,4,2',4',5'	54
17.35(R)	1	0.52	2,4,5,2',4',5'*+ 3,4,2',3',4'	54
18.56	23	0.31	2,3,4,2',4',5'*	54 + 60
19.25	24	0.59	Cl_5	60
20.05	25	0.27	2,3,4,2',3',4'+ 2,3,4,2',3',4',6'	54 + 60
23.45	26	0.20	Mirex	Mirex
25.42	27	0.22	2,4,5,2',3',4',5'	60
27.93	28	0.14	Cl_6	60

NOTE: * = pure compound obtained from Analabs, Inc. (North Haven, Conn.); † = pure compound obtained from RFR Corp. (Hope, R.I.).



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ID: 41577 BOTTLE 9
ESTD

RT	EXP RT	AREA	CAL #	AMT
2.78	2.78	239500	2	1.452
4.16	4.15	108600	3	1.530
6.63	6.62	1090000	4	0.881
7.72	7.71	396500	5	0.542
7.94	7.93	297300	12	0.001
8.26	8.25	324300	6	0.479
8.57	8.57	283700	7	0.419
9.08	9.08	63700	19	0.001
10.00	10.00	2416000	8	1.948
10.45	10.45	1544000	9	0.370
11.33	11.33	784200	11	0.332
11.79	11.79	784200	13	0.409
12.23	12.23	193800	14	0.301
12.50	12.50	1093000	15	0.602
13.04	13.04	2438000	16	0.339
13.69	13.68	1016000	17	0.248
14.15	14.15	3521000	18	1.770
14.75	14.74	2228000	20	0.963
15.67	15.66	1250000	21	0.393
16.25	16.24	2361000	22	1.131
17.00	17.00	5470000	(R) 1	0.525
18.23	18.23	6408000	23	0.315
19.68	19.66	3721000	25	0.202
22.75	22.76	[illegible]	26	0.229
24.72	24.72	4139000	27	0.223
27.26	27.26	3228000	28	0.378

DIL FACTOR: 1.0000 E+ 0

FIGURE 2. *EC chromatogram of PCB standard, 4 μg/ml each of Aroclors 1016, 1221, 1254, and 1260.*

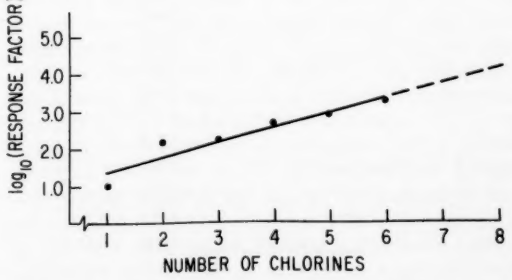


FIGURE 3. *Plot of $\log_{10}$ (response factor) versus number of chlorine atoms on biphenyl.*

homogenate with each of the four Aroclor mixtures, in triplicate. A 100-μl acetone solution of the Aroclor (100 μg/ml) was slowly added as the portion was re-homogenized, thus yielding a concentration in the spiked portion of 2.0 μg/g (wet weight) of the particular Aroclor. Each spiked portion was prepared and analyzed in the same manner as were the samples. The spike recoveries for some major peaks in the four Aroclor mixtures are reported in Table 2. All results are uncorrected for recovery.

Sample concentrations were entered into a PDP 11/45 computer which summed the concentrations and applied the dilution factors, producing a for-

TABLE 2. *Spike recoveries for some major peaks in four Aroclor mixtures*

Aroclor	Peak Component	% Recovery Replicate 1	2	3	Average
1221	2	33	33	26	31
	2,2'+4	40	40	43	41
	2,4'	51	49	51	50
1016	2,4'	35	37	35	36
	2,2',5'	52	52	50	51
	Cl_3	77	80	78	78
	2,3,2',5'+2,3,2',5'	95	101	94	97
1254	2,5,2',5'+2,3,2',5'	79	79	79	79
	Cl_4	77	87	87	84
	2,5,2',3',6'	73	74	74	74
	2,5,3',4'	96	93	96	95
	2,5,2',4',5'	72	71	71	71
	2,3,4,2',3',6'	72	72	72	72
	2,4,5,2',4',5'+3,4,2',3',4'	65	66	66	66
	2,3,4,2',4',5'	68	68	65	67
	2,3,4,2',3',4'+2,3,4,2',3',4',6'	65	71	77	71
1260	2,5,2',3',6'	77	80	80	79
	2,5,2',4',5'	70	81	76	76
	2,3,4,2',3',6'	70	78	74	74
	2,4,5,2',4',5'+3,4,2',3',4'	66	77	69	71
	2,3,4,2',4',5'	66	73	69	69
	2,3,4,2',3',4'+2,3,4,2',3',4',6'	66	74	65	68
	2,4,5,2',3',4',5'	61	67	62	63
	Cl_8	64	71	67	67

matted report (Fig. 4). *p,p'*-DDE was estimated from the 2,5,2',3',4'-pentachlorobiphenyl peak by assuming that its ratio with the 2,5,3',4'-tetrachlorobiphenyl peak was constant at 1.05:1.00. The following formula was used:

$$\mu g\ p,p'\text{-DDE/g} = \left(A_1 - \frac{A_2}{1.05}\right) \times 0.196 \times 10^{-6}$$

Where A_1 is the area of the 2,5,2',3',4'-pentachlorobiphenyl peak; A_2 is the area of the 2,5,3',4'-tetrachlorobiphenyl peak; and the constant represents the response coefficient of the *p,p'*-DDE peak at a concentration of 1.7 μg/ml. Since the relevant PCB concentrations are usually small compared to the *p,p'*-DDE concentration, the approximation was fairly good, with a detection limit of 0.1 μg *p,p'*-DDE/ml. The residual pentachlorobiphenyl concentration was included in the sum to obtain the total PCB concentration. As a quality control, solutions designed to mimic the common concentrations of PCBs in fish were analyzed frequently to test detector and integrator responses. These quasi-fish contained 4 μg Aroclor 1016/ml, 8 μg 1254/ml, 4 μg 1260/ml, and 0.33 μg mirex/ml. The detection limit was 0.5 ng total PCB, which corresponds to 0.2 μg/g (wet wt) in the fish.

SAMPLE: 4:4:4:4 (1016:1221:1254:1260) PCB STND

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.525
2	2	1.452
3	2,2' & 4	1.530
4	2,4'	.801
5	2,2',5'	.542
6	2,2',4'	.476
7	2,2',3'	.419
8	CL3	1.940
9	2,5,2',5' & 2,3,2',5'	.370
11	CL4	.332
13	2,5,2',3',6'	.409
14	CL4	.301
15	2,5,3',4'	.602
16	2,5,2',4',5'	.339
17	2,5,2',3',4'	.248
18	2,3,4,3',6' & CL6	1.770
20	2,3,6,2',4',5'	.963
21	2,3,4,2',3',6'	.393
22	3,4,2',4',5'	1.131
23	2,3,4,2',4',5'	.315
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.282
26	MIREX	.229
27	2,4,5,2',3',4',5'	.223
28	CL8	.378
	TOTAL	15.970

FIGURE 4. *Computer output for PCB standard, 4 μg/ml each of Aroclors 1016, 1221, 1254, and 1260.*

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The 8.0-ml aliquots of extracts for 13 shad from each site were pooled to form two samples, which were concentrated to 26 ml. For each composite sample, 13 columns containing 10.0 g of 2 percent deactivated Florisil and 2.0 g sodium sulfate were set up. Two ml of the concentrated composite was applied to each column and eluted with hexane. Forty ml of eluate was collected from each column, recombined, and concentrated to 2 ml. After the initial cleanup, the final 2 ml was passed through a column containing 10.0 g activated Florisil and 2.0 g sodium sulfate, and eluted with hexane. Ten 5-ml fractions were collected and each was concentrated to 0.1 ml and analyzed separately by GC/MS.

Analyses were performed on a Finnigan gas chromatograph/mass spectrometer/Data System Series 9500/1015D/6000. Instrument parameters and operating conditions were as follows:

Gas chromatograph:	
injection volume	5 µl
column	glass, 5 ft long by 2 mm id packed with 2 percent Apiezon L on Ultrabond
temperature	190°C
Mass spectrometer:	
ionization energy	70 eV
emission current	400 µamp
pre-amp sensitivity	10^{-6} amp/volt
instrument range	H
Data system:	
mass range	100–500
integration time	10
seconds per scan	4

The detection limit was 5 ng 2,4′-dichlorobiphenyl and 200 ng Aroclor 1254.

Results

Table 3 lists the quantitative results of EC–GC for PCBs. Because the correlation between length and PCB concentration was investigated, the lengths of the shad are also listed. Those fish with a PCB concentration or a length different by more than 2 SD from the mean were excluded from further computations, and the means were recalculated. Mean PCB concentrations from the two sites were compared using Student's *t*-test, assigning a significance level of 1 percent and without assuming equal variability of the two groups (*9*). The lengths were treated in a similar manner. Both were found to differ. The mean PCB concentration for shad from the Tappan Zee site (HRM 27) was 2.0 ± 1.0 µg/g, wet weight, and for shad from the Poughkeepsie site (HRM 75), the mean PCB concentration was 6.1 ± 2.6 µg/g, wet weight. The mean length of HRM 27 fish was 48.2 ± 3.0 cm, and of HRM 75, 52.9 ± 4.4 cm. The average length of the upriver fish is about 10 percent greater, whereas the average PCB concentration is nearly three times higher. There is only a weak positive correlation within each group between length and PCB concentration. The coefficient for HRM 27 is +0.40, and for HRM 75, +0.50. Chromatograms of a 16-ppm standard, a 16-ppm quasi-fish, and fish No. 2C–9757 are shown in Figures 2, 5, and 6, and computer outputs for the same samples are shown in Figures 4, 7, and 8. PCB concentrations are recorded by component, as listed in Table 1. Using the algorithm described above, no *p,p′*-DDE was quantitated.

The 25 shad further analyzed by GC/MS were chosen at random and are listed in Table 4. The PCB concen-

TABLE 3. *Length of and total PCB concentration in American shad from the Hudson River, spring 1977*

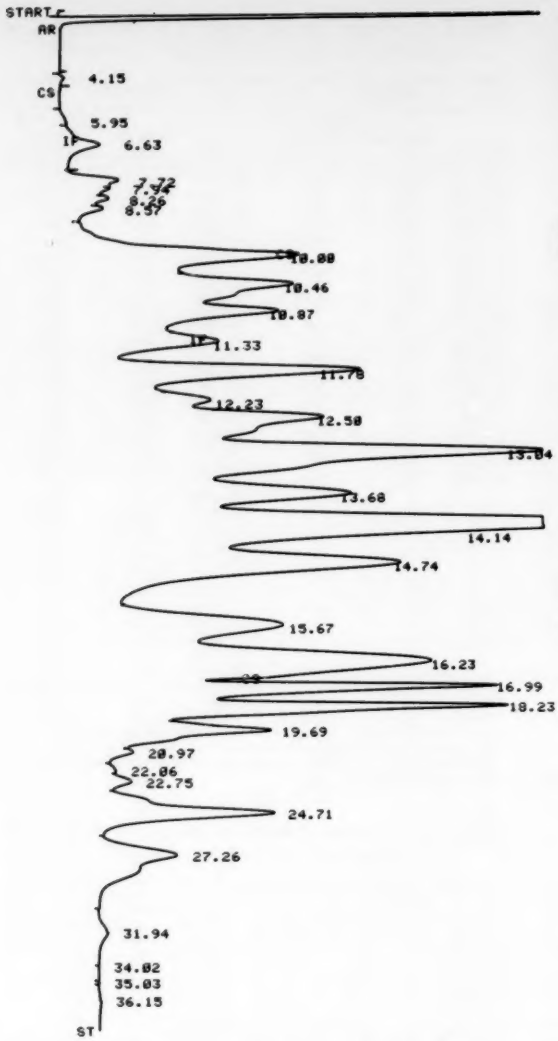
HRM 27 [1]			HRM 75 [2]		
Tag No.	Length, cm	Total PCB Concn., µg/g wet wt	Tag No.	Length, cm	Total PCB Concn., µg/g wet wt
2C–9776	50.8	11.7 [3]	2C–9214	50.0	5.8
2C–9779	48.3	1.1	2C–9215	44.7	5.6
2C–9780	47.0	2.6	2C–9216	49.5	2.7
2C–9781	43.4	2.5	2C–9221	51.6	2.4
2C–9782	54.1	5.5	2C–9222	50.5	2.4
2C–9783	43.2	1.5	2C–9223	51.6	6.9
2C–9784	43.7	2.3	2C–9224	46.7	1.9
2C–9785	45.7	2.0	2C–9225	49.5	6.1
2C–9786	50.8	2.1	2C–9226	47.0	3.3
2C–9787	46.2	1.4	2C–9227	55.6	6.4
2C–9788	45.7	0.9	2C–9228	49.5	2.3
2C–9789	50.8	1.8	2C–9229	49.3	11.2
2C–9790	49.5	1.2	2C–9230	51.1	8.7
2C–9791	50.8	2.0	2C–9231	61.0	6.7
2C–9792	48.8	1.2	2C–9232	50.5	6.3
2C–9793	45.7	1.3	2C–9233	55.4	6.4
2C–9794	47.0	1.6	2C–9234	62.2	12.2
2C–9795	50.8	1.7	2C–9753	58.7	16.1 [3]
2C–9797	48.3	3.1	2C–9754	51.6	4.4
2C–9798	50.8	2.4	2C–9755	53.3	7.7
			2C–9756	54.6	7.3
			2C–9757	55.9	6.3
			2C–9758	54.6	9.0
			2C–9759	40.6 [3]	5.3
			2C–9760	54.6	7.6
			2C–9761	55.9	19.0 [3]
			2C–9762	54.6	4.3
			2C–9763	48.3	4.2
			2C–9764	56.6	9.4
			2C–9765	54.6	4.2
			2C–9766	57.2	8.6
			2C–9767	52.1	6.3
Mean	47.9	2.0	Mean	52.9	6.1
±SD	±3.1	±1.0	±SD	±4.4	±2.7

[1] Tappan Zee site, 27 miles from the mouth of the Hudson River.
[2] Poughkeepsie site, 75 miles from the mouth of the Hudson River.
[3] Over 2 SD difference.

TABLE 4. *American shad from Hudson River analyzed additionally by GC/MS, spring 1977*

HRM 27 [1]		HRM 75 [2]	
Tag No.	PCB Concn., µg/g	Tag No.	PCB Concn., µg/g
2C–9776	11.7	2C–9216	2.7
2C–9781	2.5	2C–9222	2.4
2C–9782	5.5	2C–9224	1.9
2C–9783	1.5	2C–9225	6.1
2C–9784	2.2 (twice)	2C–9228	2.3
2C–9784	2.3	2C–9229	11.2
2C–9786	2.1	2C–9754	4.4
2C–9787	1.4	2C–9755	7.7
2C–9790	1.2	2C–9756	7.3
2C–9793	1.3	2C–9757	6.3
2C–9795	1.7	2C–9759	5.3
2C–9797	3.1	2C–9761	19.0
2C–9798	2.4	2C–9767	6.3
Mean	3.0	Mean	6.4

[1] Tappan Zee site, 27 miles from the mouth of the Hudson River.
[2] Poughkeepsie site, 75 miles from the mouth of the Hudson River.



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ID: 41577 BOTTLE 10
ESTD

RT	EXP RT	AREA	CAL #	AMT
4.15	4.15	37960	3	0.542
6.63	6.62	501700	4	0.356
7.72	7.71	419600	5	0.561
7.94	7.93	309700	12	0.001
8.26	8.25	331500	6	0.491
8.57	8.56	246200	7	0.364
10.00	9.99	2492000	8	2.032
10.46	10.44	2126000	9	0.589
11.33	11.32	850600	11	0.411
11.78	11.78	1253000	13	0.591
12.23	12.22	367800	14	0.437
12.50	12.49	1860000	15	0.953
13.04	13.03	4217000	16	0.571
13.68	13.68	2026000	17	0.479
14.14	14.14	5800000	18	2.000
14.74	14.74	2990000	20	1.248
15.67	15.66	1767000	21	0.551
16.23	16.24	4346000	22	2.062
16.99	17.00	8020000	(R) 1	0.763
18.23	18.21	8704000	23	0.421
19.69	19.66	4372000	25	0.317
22.75	22.73	484900	26	0.386
24.71	24.70	5020000	27	0.263
27.26	27.24	3580000	28	0.156

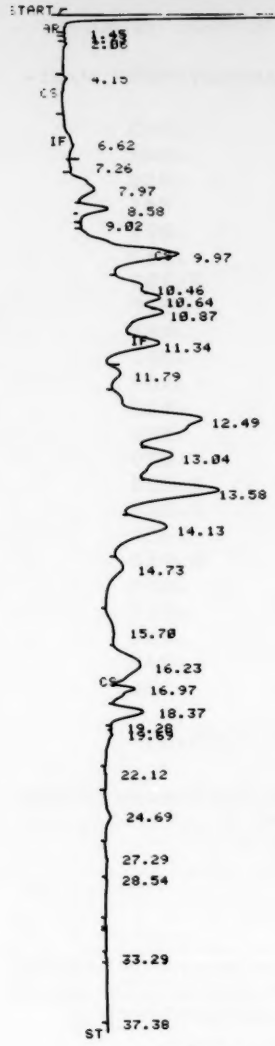
DIL FACTOR: 1.0000 E+ 0

FIGURE 5. *EC chromatograms of PCB quasi-fish: 4 μg/ml each of Aroclors 1016 and 1260; 8 μg/ml Aroclor 1254; and 0.33 μg/ml mirex.*

tration mean did not differ significantly from the respective group means, as determined by the statistical test described above. The compounds identified by MS are listed in Table 5. Nonpolar compounds, which usually interfere with MS determinations of PCBs, elute first from the Florisil column. The alkane series, from C_{22} to C_{26}, were collected in fraction 1. The peaks in the total ion chromatograms (Fig. 9) are quite broad, indicating a mix of isomers for each alkane. PCBs from trichloro- through pentachloro-, were collected in fractions 3–7 (Fig. 10). Consistent with the EC–GC analysis, more PCB components were detected in the fish collected up-river. A notable exception is the polar trichlorobiphenyls detected in fraction 27–7. DDE, which is difficult to quantitate by EC–GC because it tends to overlap a PCB peak, as explained above, was only observed in the fish from HRM 75 (Fig. 11), apparently in a concentration below the EC–GC detection limit.

Discussion

Fractionation of the cleaned extract on activated Florisil aids in the analysis of fish for pesticides and PCBs. The mass spectrometer analyzing chamber does not become



HP RUN # 12 JUN/26/77 TIME 01:45:46
ID: 41577 BOTTLE 12
ESTD

RT	EXP RT	AREA	CAL #	AMT
4.15	4.15	117800	3	1.681
6.62	6.61	61530	4	0.044
7.97	7.92	427700	12	0.001
8.58	8.55	390800	7	0.579
9.02	9.06	51970	19	0.001
9.97	9.98	1487000	8	1.213
10.46	10.43	365300	9	0.088
10.64	10.63	429700	10	0.264
11.34	11.31	454900	11	0.220
11.79	11.76	55010	13	0.026
12.49	12.47	1218000	14	0.624
13.04	13.01	717600	16	0.097
13.58	13.66	1028000	17	0.243
14.13	14.12	651800	18	0.315
14.73	14.72	179000	20	0.075
15.70	15.64	89420	21	0.028
16.23	16.22	486700	22	0.231
16.97	17.00	618900	(R) 1	0.059
18.37	18.19	873200	23	0.042
19.28	19.30	40840	24	0.017
19.69	19.64	164700	25	0.012
24.69	24.67	169600	27	0.009
27.29	27.21	53760	28	0.002

DIL FACTOR: 1.0000 E+ 0

FIGURE 6. *EC chromatogram of American shad No. 2C-9757, Hudson River, spring 1977.*

contaminated, thus the background noise is reduced. The chromatograms are simplified; DDE does not overlap a PCB peak, which facilitates quantitation of both. If DDE were present at a higher concentration, as is the case in fish from Lake Ontario which have concentrations ranging from 1 ppm to 5 ppm (Brian Bush, 1977, personal communication), the DDE would be quantitated by the method described above.

Shad were analyzed in 1975 by DEC (*11*) during a statewide monitoring program. Fifteen shad were collected in the lower Hudson River as far upstream as Coxsackie/Catskill. The sites were not specifically identified in the report. Several of the fish samples were pooled, so that there were six composites analyzed. Results were reported in terms of the Aroclor 1242/1016 and Aroclor 1254 averages, namely 1.35 ppm and 1.14 ppm wet weight, respectively, for an overall average of 2.49 ppm. This is close to the overall average of 5.1 ppm obtained in the present study, although there is not sufficient data for full statistical comparison.

The American shad seems to be a good species of fish with which to monitor water pollution of a river system. The shad ranges throughout the eastern seaboard. It is large enough and of sufficient number to be collected easily and without impairing its population. Direct water analyses are difficult to perform. The only PCB concen-

SAMPLE: 4:8:4 (1016:1254:1260) PCB QUASI-FISH

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.763
3	2,2' & 4	.542
4	2,4'	.356
5	2,2',5'	.561
6	2,2',4'	.491
7	2,2',3'	.364
8	CL3	2.032
9	2,5,2',5' & 2,3,2',5'	.509
11	CL4	.411
13	2,5,2',3',6'	.591
14	CL4	.437
15	2,5,3',4'	.953
16	2,5,2',4',5'	.571
17	2,5,2',3',4'	.479
18	2,3,4,3',6' & CL6	2.800
20	2,3,6,2',4',5'	1.248
21	2,3,4,2',3',6'	.551
22	3,4,2',4',5'	2.062
23	2,3,4,2',4',5'	.421
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.317
26	MIREX	.386
27	2,4,5,2',3',4',5'	.263
28	CL8	.156
	TOTAL	16.878

FIGURE 7. *Computer output for PCB quasi-fish, 4 μg/ml each of Aroclors 1016 and 1260, 8 μg/ml Aroclor 1254, and 0.33 μg/ml mirex.*

trations reported in Hudson River waters, from the Troy and Poughkeepsie areas, are in the range of 0.11–1.1 ppb (*6*) which strains the limit of detection. As mentioned in the introduction, shad do not eat in fresh water before spawning. Therefore, any contaminants they contain are due to their ocean feeding or are assimilated directly from the river water. An indication of the water contamination between the river mouth and the point of collection is obtained. This information could not be obtained as conveniently by other means.

There is a chance that the few fish having PCB concentrations significantly higher than the mean levels are repeat spawners (Ronald Sloan, 1979, DEC; private communication). Talbot (*12*) in 1954 estimated that 51 percent of the shad return to spawn again in the Hudson River. This is probably a high estimate, because in 1975 Chittenden (*3*) measured a repeat rate of only 3 percent in the Delaware River. Shad in more southern rivers spawn only once (*13*). The chance of repeat spawners did not prevent the observation of a significant increase in contamination levels in the fish collected up-river, even with only a small sampling.

In addition to the use of these fish for monitoring river contamination, the shad are important in their own right. The Hudson River shad fishery is being redeveloped. The New York State legislature, with the support of the National Oceanic and Atmospheric Administration, administered a study of the fishery (*8*). At that time, the major concerns were over-fishing and low oxygen supply in the river mouth. Those problems have been corrected, and the shad population is increasing. The annual festival held in April to celebrate the shad run has been revitalized. In July 1979, the State Environmental Conservation law was amended to establish a fishery management program for the tidal portion of the Hudson River (i.e., as far north as Troy, New York). The fish should be analyzed periodically as a check on their quality and as an indication of water quality.

SAMPLE: 2C-9757

-PEAK-	-COMPONENT-	-AMOUNT (PPM W/W)-
1	2,4,5,2',4',5' & 3,4,2',3',4'	.089
3	2,2' & 4	.020
4	2,4'	.066
7	2,2',3'	.869
8	CL3	1.819
9	2,5,2',5' & 2,3,2',5'	.132
10	2,3,2',3'	.396
11	CL4	.330
13	2,5,2',3',6'	.039
14	CL4	.936
16	2,5,2',4',5'	.146
17	2,5,2',3',4'	.365
18	2,3,4,3',6' & CL6	.473
20	2,3,6,2',4',5'	.113
21	2,3,4,2',3',6'	.042
22	3,4,2',4',5'	.347
23	2,3,4,2',4',5'	.063
24	CL7	.025
25	2,3,4,2',3',4' & 2,3,4,2',3',4',6'	.018
27	2,4,5,2',3',4',5'	.013
28	CL8	.003
	TOTAL	6.304

FIGURE 8. *Computer output for American shad No. 2C-9757, Hudson River, spring 1977.*

TABLE 5. *Identification of compounds, by fraction, found in composites of American shad from the Hudson River, spring 1977*

HRM 27 Composite [1]			HRM 75 Composite [2]		
Fraction	Scan No.	Compound	Fraction	Scan No.	Compound
27–1	60	Docosane	75–1	12	Pristane
	88	Tricosane		59	Docosane
	129	Tetracosane		85	Tricosane
	194	Pentacosane		125	Tetracosane
	286	Hexacosane		187	Pentacosane
				276	Hexacosane
27–3	47	Trichlorobiphenyl	75–3	50	Tetrachlorobiphenyl
27–4	53	Tetrachlorobiphenyl	75–4	52	Tetrachlorobiphenyl
	65	Tetrachlorobiphenyl		79	Pentachlorobiphenyl
	118	Tetrachlorobiphenyl		101	Pentachlorobiphenyl
27–5	30	Trichlorobiphenyl	75–5	28	Trichlorobiphenyl
	50	Trichlorobiphenyl		37	Trichlorobiphenyl
	56	Tetrachlorobiphenyl		46	Trichlorobiphenyl
	99	Tetrachlorobiphenyl		73	Tetrachlorobiphenyl
	108	Tetrachlorobiphenyl		99	Tetrachlorobiphenyl
	148	Pentachlorobiohenyl		119	DDE
				136	Pentachlorobiphenyl
				219	Pentachlorobiphenyl
27–6	54	Trichlorobiphenyl	75–6	29	Trichlorobiphenyl
	78	Tetrachlorobiphenyl		35	Trichlorobiphenyl
				53	Trichlorobiphenyl
				73	Tetrachlorobiphenyl
				160	Pentachlorobiphenyl
27–7	31	Trichlorobiphenyl	75–7	83	Tetrachlorobiphenyl
	39	Trichlorobiphenyl			
	86	Tetrachlorobiphenyl			

[1] Twelve fish from Tappan Zee site, 27 miles from the Hudson River mouth.

[2] Thirteen fish from Poughkeepsie site, 75 miles from the Hudson River mouth.

Acknowledgments

The authors wish to thank the following persons from the New York State Department of Health, Division of Laboratories and Research: Maria Mahar and Mary Ellen Murphy for technical assistance on this project and Paul Turner for computer assistance.

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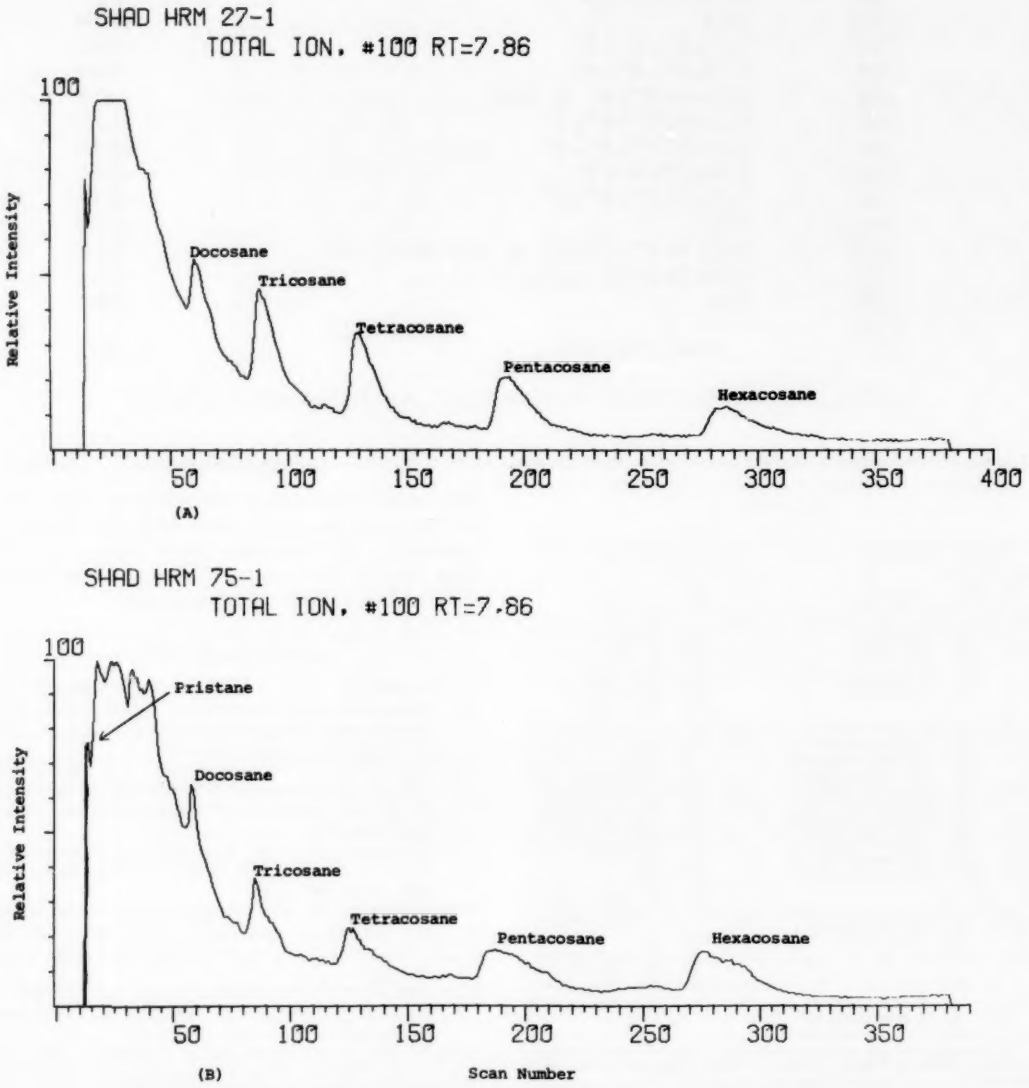

FIGURE 9. *MS total ion chromatograms for (a) Fraction No. 27-1 and (b) Fraction No. 75-1.*

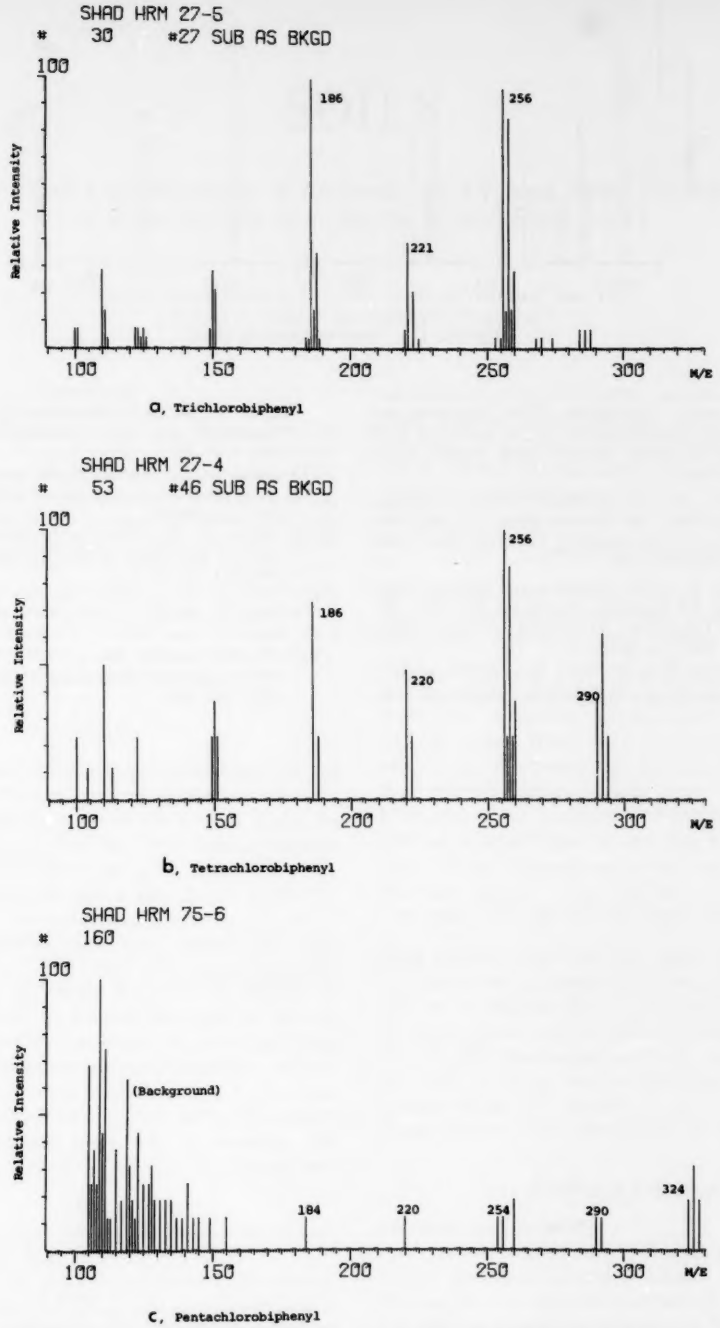

FIGURE 10. *Mass spectra of (a) trichlorobiphenyl, (b) tri- and tetrachlorobiphenyls, and (c) pentachlorobiphenyl.*

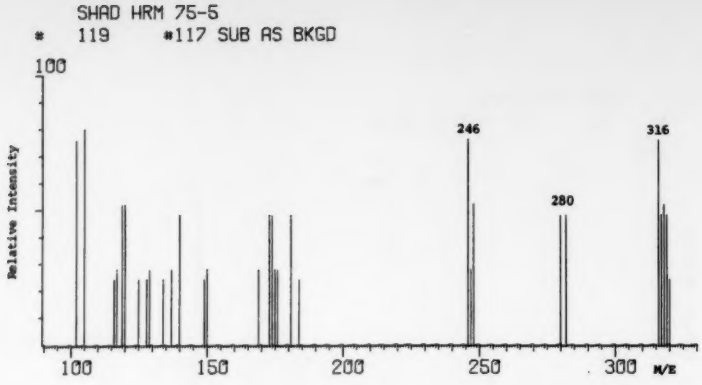

FIGURE 11. *Mass spectrum of DDE.*

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SOILS

Residual Concentrations of Propanil, TCAB, and Other Pesticides in Rice-Growing Soils in the United States, 1972

Ann E. Carey,[1] Henry S. C. Yang,[1] G. Bruce Wiersma,[2] Han Tai,[3]
Robert A. Maxey,[3] and Aubrey E. Dupuy, Jr.[3]

ABSTRACT

Ninety-nine soil samples from the rice-growing states of Arkansas, California, Louisiana, Mississippi, and Texas were collected, primarily to monitor the herbicide propanil. No residual concentrations of propanil were detected in any of these samples, but TCAB, a propanil transformation product, was detected in six samples at concentrations ranging from 0.01 ppm to 0.05 ppm. Organochlorine and organphosphorus pesticide determinations were also performed. The compounds dieldrin, aldrin, and DDT and its metabolites were found more frequently; endrin and chlordane were found less frequently. The organophosphorus pesticides diazinon and parathion were detected occasionally.

Introduction

Since 1961, propanil (3',4'-dichloropropionanilide) has been used as a selective, post-emergence herbicide in the major, rice-growing areas of the United States. In the past few years, propanil has been studied because some of its transformation products have chemical structures similar to those of carcinogens (*1, 2, 4, 5, 15*). The formation of azobenzene compounds in soils where aniline-based herbicides have been applied has been documented (*5, 9*). The formation of these compounds from propanil has also been shown to be affected by other pesticides (*10*), by the nutrient status of the soil (*13*), and by physical conditions (*3*). Most of these data have been determined through laboratory studies, but the formation of these azobenzenes has also been documented in limited field studies (*12*). The major objective of the present study was to determine the concentrations of propanil, TCAB (3,3',4,4'-tetrachloroazobenzene, a transformation product of propanil), and other selected organochlorine and organophosphorus pesticides in soil and rice under actual use conditions. All of the soil analyses were completed and only those results are reported here.

Sampling Procedures

Soil samples were collected during late summer 1972 from 99 sites located in Arkansas, California, Louisiana, Mississippi, and Texas. The number of sampling sites within states and counties was proportional to the amount of land used for rice production in those areas. Each site represents approximately 6,073 hectares (15,000 acres). When more than one site was allocated to a county, the county was divided into quadrants, and the required number of sites were randomly selected from among the quandrants. Field personnel were instructed to select fields for sampling where propanil had been applied. Information on the kinds and amounts of pesticides applied to the sampling sites was obtained in a personal interview with the landowner or operator.

Each sampling site was 231 square meters, usually a 15.2 meter by 15.2 meter plot, from which 16 soil cores (5.1 cm in diameter by 7.6 cm deep) were collected on an evenly spaced, 4 x 4 grid. A detailed description of the sampling technique has been reported previously (*9*). The 16 cores were composited, sifted through a 6.3-mm sieve, and shipped to the Toxicant Analysis Center, Bay St. Louis, Mississippi, for analysis.

Analytical Procedures

PROPANIL AND TCAB

From the thoroughly mixed field sample, a 100-g subsample was weighed into a 500-ml Erlenmeyer flask. The sample was extracted by shaking with 200 ml of a 1:1 mixture of acetone:benzene for 2 hr on a reciprocating shaker. The supernatant liquid was decanted into

[1] Field Studies Branch, Survey and Analysis Division, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, TS-793, Washington, D.C. 20460.
[2] Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Las Vegas, Nev.
[3] Toxicant Analysis Center, Survey and Analysis Division, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, National Space Technology Laboratory, Bay St. Louis, Miss. 39529.

a 500-ml separatory funnel and washed three times with 100-ml portions of distilled water to remove the acetone. The benzene extract was dried with anhydrous sodium sulfate and concentrated 10:1 for determination of propanil and TCAB.

Determinations were performed on gas chromatographs equipped with tritium foil electron-affinity detectors. Instrument parameters and operating conditions were as follows:

Gas chromatographs:	Micro Tek 220	
Columns:	Glass, 183 cm long, 6 mm OD by 4 mm ID, packed with one of the following: 3 percent DC-200 on 100–120-mesh Gas-Chrom Q; a mixture of 1.5 percent OV-17 and 1.95 percent OV-210 on 100–120-mesh Supelcoport; or 10 percent DC-200 on 100–120-mesh Gas-Chrom Q	
Temperatures, °C:	detector	200
	injection port	250
	DC-200 columns	195
	mixed column	195
Carrier gases:	5 percent methane in argon flowing at 80 ml/minute	

Propanil and TCAB were identified on the 3 percent DC-200 column with an electron-capture detector. Minimum detectable levels of residues were 0.005 ppm propanil and 0.20 ppb TCAB. Identity was confirmed on the 3 percent mixed column by EC detector; minimum detectable levels were comparable to those on the DC-200 column. Additional confirmation was accomplished with a Dohrmann microcoulometric detector in the halogen mode, on a 10 percent DC-200 column. Minimum detectable levels with the microcoulometric detector were 0.025 ppm propanil and 0.02 ppm TCAB. Recovery averaged 90 percent for propanil and 86 percent for TCAB. All concentrations reported in the tables were corrected for recovery, and were converted to a dry weight basis.

ORGANOCHLORINE AND ORGANOPHOSPHORUS PESTICIDES

The analytical method for determining organochlorine and organophosphorus pesticides has been described previously (*10*). Minimum detectable levels for organochlorines and trifluralin were 0.002–0.03 ppm except for combinations of polychlorinated biphenyls (PCBs), chlordane, toxaphene, and other compounds which had minimum detectable levels of 0.05–0.1 ppm. Minimum detectable levels for organophosphates were 0.01–0.03 ppm. Average recoveries by this procedure were 93 percent for organochlorines and 85 percent for organophosphates. All concentrations reported in the tables were corrected for recovery and were converted to a dry weight basis.

Results and Discussion

Of the 99 sites sampled, 81 sites or 82 percent received applications of propanil ranging from 1.2 kg/ha to 11.2 kg/ha (1.1–10.0 lb/acre) during the sampling year. Ten of the 81 sites had received applications of propanil over a four-year period prior to sampling, seven sites were known to have had no propanil applications, and the pesticide use history was unknown for 11 sites.

The results obtained for propanil and TCAB are presented in Table 1. No residue of propanil was detected in any of the 99 soil samples analyzed, but six of the 99 samples (6.1 percent) contained TCAB. TCAB concentrations ranged from 0.01 ppm to 0.05 ppm. These results indicate that the frequency of occurrence and residue concentrations of TCAB are probably quite low.

The results of analyses of soil samples for organochlorine and organophosphorus pesticides are shown in Table 2. Dieldrin, aldrin, and DDT and its metabolites were found most frequently; endrin and chlordane, less frequently. The organophosphorus pesticides diazinon and parathion were detected occasionally. Polychlorinated biphenyls (PCBs) were detected in one soil sample from Arkansas.

The occurrence of organochlorine residues in the rice-growing region is generally similar to that reported by other residue monitoring studies conducted in the same region (*7, 8*).

TABLE 1. *Concentrations of propanil and ACTB in soils from rice-growing areas of the United States, 1972*

State	No. of Samples	% Positive Samples		Residues, ppm Dry wt			
		Propanil	TCAB	TCAB Arithmetic Mean	TCAB Positive Arithmetic Mean [1]	Detected Values Min.	Max.
Arkansas	24	ND	12.5	0.01	0.01	0.01	
California	19	ND	5.3	0.01	0.01	0.01	
Louisiana	28	ND	7.1	0.01	0.03	0.01	0.05
Mississippi	3	ND	ND	—	—		
Texas	25	ND	ND	—	—		
All states	99	ND	6.1	0.01	0.02	0.01	0.05

NOTE: ND = Not detected.
[1] Positive arithmetic mean = Sum of concentrations of positive samples/number of positive samples.

TABLE 2. *Concentrations of organochlorine and organophosphorus compounds in soils from rice-growing areas of the United States, 1972*

State	No. of Samples	Residues, ppm Dry wt											
		Dieldrin	Aldrin	Endrin	Chlordane	Diazinon	Parathion	PCBs	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-TDE	ΣDDT
Arkansas	24												
Range of detected residues [1]		0.01–0.27	0.01–0.25	ND	ND	ND	0.12	1.13	0.01–0.09	0.02	0.01–0.57	0.01–0.21	0.01–0.57
Arithmetic mean		0.08	0.03	—	—	—	0.01	0.05	0.02	<0.01	0.05	0.03	0.09
% Positive samples		95.8	62.5	—	—	—	4.2	4.2	37.5	4.1	33.3	41.7	54.1
California	19												
Range of detected residues		0.01–0.06	0.01	0.17	ND	ND	0.01	ND	0.01–0.25	ND	0.01–0.15	0.01–0.39	0.01–0.39
Arithmetic mean		0.01	<0.01	<0.01	—	—	<0.01	—	0.02	—	0.05	0.01	0.17
% Positive samples		52.6	5.3	5.3	—	—	10.5	—	52.6	—	89.5	89.5	89.4
Louisiana	28												
Range of detected residues		0.01–0.16	0.01–0.07	ND	0.01–0.27	ND	ND	ND	0.02–0.44	ND	0.02–0.25	0.08–0.94	0.02–0.94
Arithmetic mean		0.04	<0.01	—	0.01	—	—	—	0.02	—	0.01	0.04	0.06
% Positive samples		89.3	25.0	—	7.1	—	—	—	10.7	—	7.1	7.1	7.1
Texas	25												
Range of detected residues		0.01–0.10	0.02–0.12	ND	0.02–0.21	0.01–0.06	ND	ND	0.03–0.06	ND	0.01	0.02	0.01–0.06
Arithmetic mean		0.03	0.02	—	0.06	0.01	—	—	<0.01	—	<0.01	<0.01	<0.01
% Positive samples		92.0	56.0	—	76.0	28.0	—	—	8.0	—	4.0	4.0	12.0
Mississippi	3												
Range of detected residues		0.01–0.09	0.05	ND	ND	ND	ND	ND	0.06–0.07	ND	0.02–0.08	0.02–0.08	0.02–0.08
Arithmetic mean		0.04	0.02	—	—	—	—	—	0.04	—	0.04	0.04	0.13
% Positive samples		100.0	33.3	—	—	—	—	—	66.7	—	100.0	100.0	100.0
All states	99												
Range of detected residues		0.01–0.27	0.01–0.25	0.17	0.01–0.27	0.01–0.06	0.01–0.12	1.13	0.01–0.04	0.02	0.01–0.57	0.01–0.94	0.01–0.94
Arithmetic mean		0.04	0.01	<0.01	0.02	<0.01	<0.01	0.01	0.02	<0.01	0.02	0.05	0.08
% Positive samples		84.8	39.4	1.1	21.2	7.8	3.3	1.1	25.3	1.1	31.3	33.3	38.4

NOTE: ND = none detected.
[1] Range does not include zero values.

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Polychlorinated Biphenyl Contamination of Areas Surrounding Two Transformer Salvage Companies, Colman, South Dakota—September 1977 [1]

Yvonne A. Greichus [2] and Barbara A. Dohman [3]

ABSTRACT

Soil, corn plants, and foliage from areas surrounding two electrical salvage companies involved in reconditioning old transformers had unusually high levels of polychlorinated biphenyls (PCBs). Levels decreased as distance from the factories increased. PCBs were dispersed into the air through incineration of waste oils; water and soil contamination was caused by runoff from the factories. PCBs found in the contaminated areas closely resembled Aroclor 1260 as did the PCBs in the waste oil, whereas PCBs in other areas were more similar to Aroclor 1254. PCBs on surface soils taken from an unplowed pasture near the factories also resembled Aroclor 1260, whereas samples taken from depths of 2–4 inches showed degradation of some PCB isomers. PCB concentrations in corn cobs and kernels were < 0.05 ppm, whereas leaves contained PCB levels of up to 2.2 ppm. PCB levels in earthworms and small rodents collected near the factories were considerably higher than levels in the same types of animals collected from other areas.

Introduction

Polychlorinated biphenyls (PCBs) have become significant environmental pollutants which are residual and toxic. Their accumulation in the food chains of many animals produces both acute and chronic effects on reproduction, growth, and behavior (*3, 6, 8*). PCBs have been used extensively in the past as a dielectric base for transformers and capacitors. Although PCBs are no longer manufactured in the United States, the U.S. Environmental Protection Agency (EPA) has estimated that, since their introduction in 1929, 1.25 billion pounds have been used. Of this amount, 60 percent is still in use and 4.4 percent has been destroyed. The rest remains in the environment (*9*). Movement of PCBs through the atmosphere has been demonstrated, and industrial or metropolitan areas are the suspected sources of the PCB contamination (*4, 7*). Ballschmiter et al. (*1*) have shown that certain isomers of PCBs occurred in the environment in the same ratios as measured in commercial PCB mixtures: Aroclors 1254 and 1260. They have presented evidence that the degradation of these isomers in the ecosphere, over 20–40 years, has been too small to produce observable changes, indicating that these isomers are extremely persistant. To further complicate matters, PCBs contain some highly toxic polychlorinated dibenzofurans (*10*). Aroclor 1254 and Aroclor 1260 contain 5.6 ppm and 2.2 ppm, respectively, of a combination of the tetra-, penta-, and hexachlorinated dibenzofurans (*5*).

When the environment has been found to be contaminated with PCBs, several important questions must be considered. If possible, the source of the contamination should be located; the method of dispersion into the environment by air, water, soil, etc., needs to be examined; and the extent of the area of pollution must be determined. Whether the contamination is of recent and/or past origin, the potential harm to the environment due to accumulation in the food chain of animals should be studied. This paper discusses an incident in which PCBs entered the environment through activities of two transformer salvage companies, and it presents methods and supporting data for answering the above questions.

Methods and Materials

During September 1977, two samples each of soil and corn leaves collected near two electrical salvage companies near Colman, South Dakota, were found to have unusually high levels of PCBs. Samples were collected in chemically cleaned glass jars or hexane-washed aluminum foil and were frozen until being analyzed. The samples were extracted and subjected to Florisil column cleanup according to the method of Greichus et al. (*2*). Instrument parameters and operating conditions for gas chromatographic analysis were as follows:

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[2] Present address: Biochemical Services Division, Rocky Mountain Geochemical Corp., Suite 343, 1400 53rd Street, Emeryville, Calif. 94608.

[3] Station Biochemistry Section, Chemistry Department, South Dakota State University, Brookings, S.D. 57007.

Gas chromatograph:	Varian Aerograph Model 2100
Detectors:	^{63}Ni and Sc-^{3}H electron-capture
Recorders:	Beckman 10-inch, 1 mv
Columns:	6-ft by ⅛-inch borosilicate glass, packed with 15 percent QF-1 silicone (Fluoro) or a 1:1 mixture of 15 percent QF-1 and 10 percent DC-200 silicone, both on 60–100-mesh Chromosorb W (HP), acid-washed and dimethylchlorosilane-treated
Carrier gas:	nitrogen flowing at 40 ml/minute
Temperatures:	column 210°C injector 220°C detector 290°C ^{63}Ni, or 250°C Sc-^{3}H

Mean recovery of PCBs from fortified samples were 90 percent ± 5 percent standard deviation for all types of samples analyzed. Residue values were corrected for percent recovery. The earlier findings of PCBs in soil and corn leaves prompted the collection of soil, corn leaves, and foliage samples up to 0.25 mile north, 2.5 miles west, and 10 miles south of the factories. Winds in that area are predominantly northwesterly in the fall and winter and southerly in the summer. The town of Colman lies to the east of the factories, and this area was not sampled.

Results and Discussion

Levels of PCBs as Aroclor 1260 on a ppm dry weight basis for the samples collected are shown in Figure 1. Highest PCB levels were found in the samples collected nearest to the factories; PCB levels became progressively lower as distance from the factories increased. An exception was soil samples taken from a drainage ditch to the west of the factory lot where levels reached 46 ppm in a low lying area.

Numerous soil, corn leaf, and foliage samples taken over a number of years from relatively noncontaminated areas of South Dakota have revealed a background level

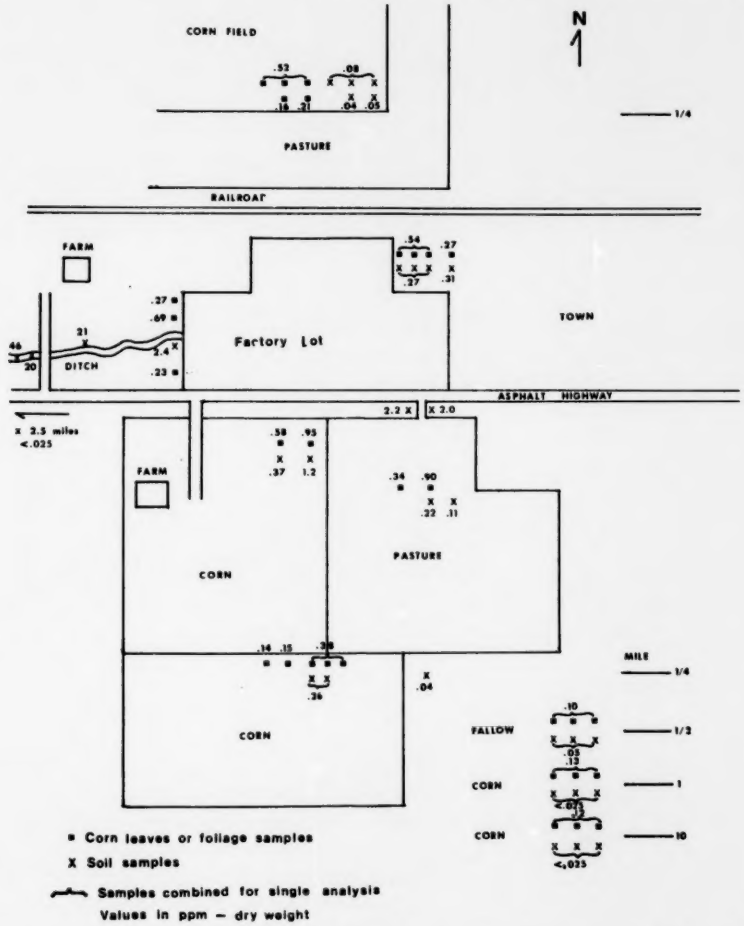

FIGURE 1. *Area surrounding Colman, South Dakota: factory lot consists of two companies adjacent to each other. ppm PCBs as Aroclor 1260.*

of < 0.1 ppm PCBs as Aroclor 1254. Therefore, the PCB levels were above expected concentrations at distances from the factories at least 0.25 mile north, less than 2.5 miles west (soil), and up to 10 miles south (corn leaves) (Fig. 1). One mile south of the factories, the soil contained < 0.025 ppm PCBs, the expected background level, although at 10 miles south of the factories, corn leaves contained 0.12 ppm PCBs, whereas the PCB levels in soil were still < 0.025 ppm, indicating airborne contamination of the leaves. This conclusion was further supported by the analysis of two entire corn plants and the soil on their roots taken 50 yards south of the factory lot (Table 1). The outer leaves contained 1.1 ppm and 2.2 ppm PCBs, the inner leaves contained 0.25 ppm and 0.34 ppm, and the kernels and cobs contained < 0.05 ppm. The 0.29 ppm and 0.53 ppm PCB levels in the roots were somewhat higher than levels in the soil on the roots, but the low levels in the stocks, cobs, and kernels did not indicate significant transport of the PCBs from the roots to the outer leaves. PCBs in the soil could be due to water drainage from one of the factories as well as from air and dust-borne material, since there was drainage from one factory into this area.

PCBs in surface soils and in corn leaves closely resembled commercial Aroclor 1260 as shown by gas chromatograms in Figure 2. The type of PCB found in waste oils (42 ppm) from one factory also resembled Aroclor 1260 (personal communication, U.S. EPA, Denver, Colo.), whereas PCBs in soils and bottom sediments

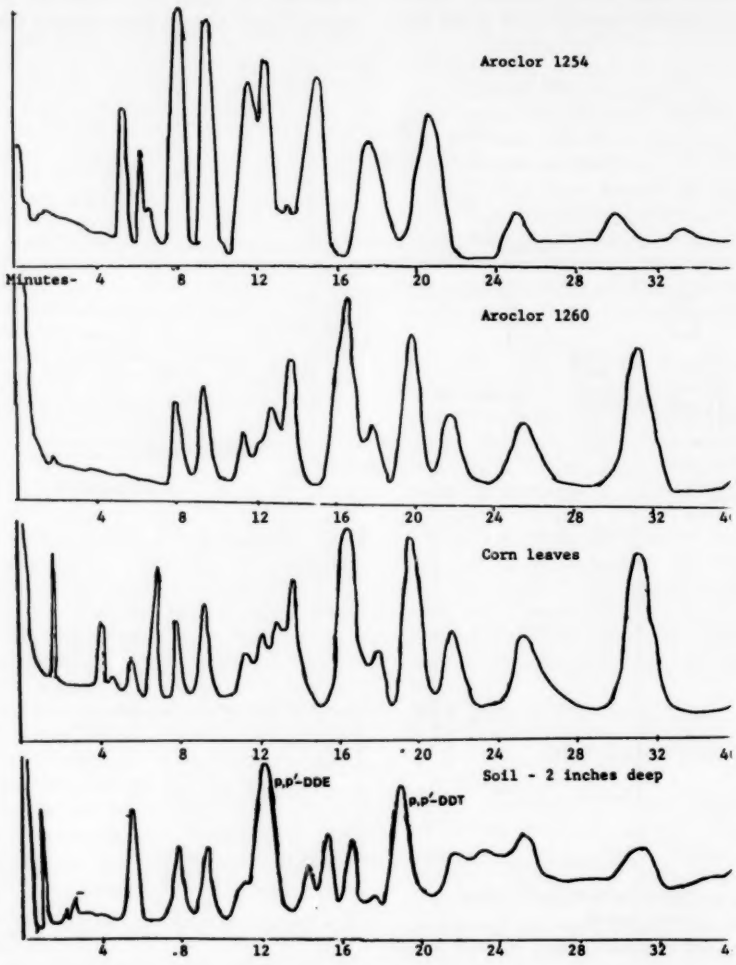

FIGURE 2. *Chromatograms of samples compared to standards of Aroclor 1254 and 1260. See text for instrument parameters and operating conditions.*

TABLE 1. *PCB levels (as Aroclor 1260) in corn plants and soil on roots, 50 yards south of the factory lot, Colman, South Dakota—September 1977*

Sample Type	PCBs, ppm Dry Wt	
	Sample No. 1	Sample No. 2
Soil on roots	0.22	0.24
Roots	0.29	0.53
Stock		
Bottom	0.12	<0.1
Middle	0.14	<0.1
Top	0.23	<0.1
Cob	<0.05	<0.05
Kernels	<0.05	<0.05
Inner leaves on ear	0.25	0.34
Leaves on plant	1.1	2.2

NOTE: Samples 1 and 2 each consists of one entire corn plant approximately 10 feet apart.

TABLE 2. *PCB levels in earthworms and rodents collected near Colman factories and in the Brookings, South Dakota, vicinity, September 1977*

Description	PCBs, ppm		
	Factory Area	Brookings Area	Ratio of Factory/ Brookings
Earthworms[1]	1.85	0.84	2.5
(*Oligochaeta terrestrial*)	2.07	0.67	
		0.54	
Vole (*Microtus* sp.)			
Liver	9.17	4.67	1.5
	4.85		
Muscle	5.68	2.60	1.7
	3.42		
Field mouse (*Peromuscus* sp.)			
Liver	9.52	2.95	4.7
	9.10	2.20	
	17.2		
Muscle	3.77	1.80	3.1
	6.87	1.72	
	5.91		
13-Lined ground squirrel (*Spermophilus* sp.)			
Liver	8.71	0.41	8.4
		1.28	
		1.44	
Muscle	2.89	0.72	3.2
		1.11	
		0.86	

[1] Each sample consisted of 2.6 g dry weight of worms.

from other areas in South Dakota did not. Soil taken at 2–4-inch depths from a pasture across the road from one factory, which had not been plowed since 1960, averaged 0.16 ppm PCBs. In the past, both factories had disposed of surplus transformer oil by incineration, and one factory used waste oil to heat the office building and the shop area (personal communication, U.S. EPA, Denver, Colo.). About four years ago, special furnaces were equipped with afterburners to destroy the PCBs. However, the presence of high levels of PCBs on the corn leaves suggests afterburners may not be efficient.

Samples taken from around one factory and analyzed by the U.S. EPA Laboratory in Denver, Colorado, contained PCBs resembling Aroclor 1260 in the following amounts: water collected from the area behind one shop building, 19 ppb; dirt from in front of an incinerator, 31 ppm; and swabs from three windows on a building next to the incinerator, 14 μg/area. There was no contamination of the Colman drinking water. Soil and vegetation taken one mile north of the factories contained 0.011 ppm PCBs. Sediment and vegetation collected about 20 ft west of a fence around one factory contained 0.17 ppm and 0.39 ppm PCBs, respectively. Soil and corn foliage taken 1 mile west of the factories, from the north side of the highway, contained < 0.02 ppm PCBs. No PCBs were detected on corn, cornstalks, and leaves taken about 1 mile east of the factories (personal communication, Food and Drug Administration, Denver, Colo.).

Earthworms and small rodents were collected from the north and south of the factories and from areas near Brookings, South Dakota, believed to be relatively free of PCBs. Earthworms near the factories and near Brookings contained average PCB levels of 1.96 ppm and 0.77 ppm, respectively, with a ratio of levels in the factory area to levels in the Brookings area of 2.5 (Table 2). PCB levels in rodents near the factories ranged from 4.85 to 17.2 ppm in liver tissues and from 3.42 to 6.87 ppm in muscle tissues. PCB levels in rodents collected near Brookings ranged from 2.20 to 4.67 ppm in liver tissues and from 1.72 to 2.60 ppm in muscle tissues.

Conclusions

The sources of the PCBs in the Colman area were related to operations involved in electrical salvage as evidenced by the predominance of Aroclor 1260 in the factory oil and in surrounding areas and by the fact that the highest levels were near the factories and became increasingly lower as the distance from the factories increased.

PCBs were dispersed by wind, water, and silt runoff in the immediate area. More distant PCB contamination was primarily airborne because PCB levels in outer corn leaves were unexpectedly high whereas soil levels were very low. Airborne contamination extended at least 0.25 mile north and 10 miles south of the factories.

The contamination was of both past and of recent origins. Levels of PCBs (Aroclor 1260) on outer corn leaves proved recent origin, and PCB levels in soil samples taken 2–4 inches deep from a pasture which had not been plowed since 1960 suggested past contamination.

Bioaccumulation is occurring because PCB levels in earthworms and small rodents collected near the factories were considerably higher than levels in the same types of animals collected from other areas.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ACEPHATE	*O,S*-Dimethyl acetylphosphoramidothioate
ALDRIN	Hexachlorohexahydro-*endo,exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1221	PCB, approximately 21% chlorine
AROCLOR 1232	PCB, approximately 32% chlorine
AROCLOR 1248	PCB, approximately 48% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
AROCLOR 1260	PCB, approximately 60% chlorine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
DBP	Dibutyl phthalate
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT); *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene; *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p'*-DDT): ă-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)2-(*p*-chlorophenyl) ethane]
DIAZINON	*O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7,-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
METHAMIDOPHOS	*O,S*-Dimethyl phosphoramidothioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene
PARATHION	*O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PROPANIL	3',4'-Dichloropropionanilide
TCAB	3,3',4,4'-Tetrachloroazobenzene
TDE	2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating.
TRIFLURALIN	α,α,α-Trifluoro-2,6-dinitro-*N,N*-dipropyl *p*-toluidine

ERRATA

PESTICIDES MONITORING JOURNAL, Volume 13, Number 4

Page 138: In the paper "Dieldrin and Heptachlor Residues in Dead Gray Bats, Franklin County, Missouri—1976 versus 1977," by D. R. Clark, Jr., R. K. LaVal, and A. J. Krynitsky, the fourth compound listed in Table 1 should be *cis*-Chlordane.

Page 148: In the paper "Organochlorine Pesticide, PCB, and PBB Residues and Necropsy Data for Bald Eagles from 29 States—1975–77," by T. E. Kaiser, W. L. Reichel, L. N. Locke, E. Cromartie, A. J. Krynitsky, T. G. Lamont, B. M. Mulhern, R. M. Prouty, C. J. Stafford, and D. M. Swineford, the second year listed in Table 4 should be 1975; the second line in the right column should read 1975–77, 20 percent (Table 5).

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